DEVELOPMENT OF COMMERCIAL, SUSTAINABLE PROCESSES FOR DYEING GENERIC, UNMODIFIED POLYPROPYLENE FIBER

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DEVELOPMENT OF COMMERCIAL, SUSTAINABLE PROCESSES FOR DYEING GENERIC, UNMODIFIED POLYPROPYLENE FIBER

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LIST OF ABBREVIATIONS

AATCC	American Association of Textile Chemists and Colorists
ASTM	American Society for Testing and Materials
CCACTI	Consortium on Competitiveness for the Apparel, Carpet and Textile Industries
C. I.	Colour Index
CIE	Commission Internationale de l'Eclairage
Cs	Concentration of Dye in Solution
Cf	Concentration of Dye in Fiber
Chempad	Chemical Pad
NIR	Near Infra Red
PP	Polypropylene
SP	Solubility Parameter
UV/Vis	Ultraviolet/ Visible

SUMMARY

A viable process for batch exhaust vat dyeing unmodified polypropylene (PP), spun yarn fabrics has been developed. Theoretical molecular dynamics simulations and solubility parameter (SP) approaches were first utilized to screen potential vat dye candidates for generic PP coloration based on their chemical structures. The correlation between dye exhaustion and the solubility parameter for PLA fiber and disperse dyes has been reported by Karst et al. [1,2] , who showed that the closer the solubility parameter of the dye was to the fiber, the better the exhaustion of the dye. Solubility parameter was calculated as the square root of the cohesive energy density.

In the case of disperse dyeing of polyester and PP, the low molecular weight dye molecule diffuses into the opened structure of the fibers at high temperatures (above their Tg's) and is physically entrapped in the fiber after cooling. A similar mechanism was projected in the case of acid leuco vat dye diffusion into the solid state structure of PP fiber. This mechanism of dye diffusion involved the solubility of the colorant molecule inside the hydrophobic fiber at elevated temperatures, and therefore acid leuco vat dyes which possessed solubility parameters closest to that of the PP fiber, coupled with low predicted energies of mixing with PP, were theorized to give greater color yields in high temperature dyeing processes.

The interactions between nonionic acid leuco vat dyes and nonpolar, generic PP fiber have been investigated in a collaborative research effort between Georgia Tech and the University of Georgia. Identification of viable vat dye candidates of a trichromatic series (compatible red, yellow and blue colorants) plus an orange based on the developed

single-stage, acid leuco vat dyeing process has been achieved with adequate fastness properties to washing, crocking and dry-cleaning: C. I. Vat Orange 1, Vat Yellow 2 and Vat Red 1 have been certified, whereas Vat Blue 6 has been demonstrated to be a marginal, though best available, candidate. The compatibility of the above colorants in mixtures has also been demonstrated by plotting their rates of dyeing in combination for light, medium and dark shades. Vat Red 1, Vat Yellow 2, Vat Blue 6 and Vat Orange 1 have shown good dyeing rate compatibility in combination. Vat Blue 1 (indigo) has also shown excellent color building and good fastness properties in PP coloration, and is thus a viable "stand alone" colorant to dye PP fabrics in the optimized, single-stage acid leuco dyeing process.

The Kebulka-Munk Equation was utilized to derive K/S values of dyed PP fabrics at the colorants' wavelengths of minimum reflectance. The K/S values were in good agreement with the predicted mixing energies of acid leuco vat dyes and PP fiber, and with the dyes' calculated SP's. The low SP/mixing energy acid leuco vat dyes (e.g., C. I. Vat Red 1) exhibited better K/S values/fastness properties on colored PP fabrics than the high SP/mixing energy vat dyes (e.g., C. I. Vat Brown 1), indicating that increasing the difference of SP between the vat dye and the PP fiber, coupled with a higher mixing energy of the dye-PP blend, results in decreased interactions between the two. For example, PP fabrics dyed with C. I. Vat Brown 1 with its high SP (19.3 $(cal/cc)^{1/2}$) and predicted mixing energy with PP (46.1 kcal/mole) exhibited a lower K/S value than those colored with the certified vat dyes, all with lower SP's and PP mixing energies.

Tensile testing of the acid leuco vat dyed PP fabrics revealed no significant impact of the developed dyeing process on the breaking loads and breaking tenacities of

the dyed samples. X-ray crystallinity diffraction patterns confirmed no significant impact of the dyeing process on the solid-state structure of the colored PP fibers. Cross-sectional micrographs of loose, dyed fibers confirmed the absence of ring-dyeing.

The developed, simulated pad-steam vat dyeing process for generic PP fabrics gave higher fabric K/S values than the analogous batch dyed fabrics for C. I. Vats Yellow 2 and Blue 1. C. I. Vat Blue 6-dyed fabrics exhibited similar color depth in both the exhaust batch and simulated pad-steam processes. Fabrics dyed with C. I. Vats Orange 1 and Red 1 by the simulated pad-steam process exhibited slightly lower K/S values than analogous fabrics colored in the exhaust batch process. The simulated pad-steam method for all dyes produced fabrics exhibiting better dye level than analogous fabrics colored by the batch exhaust method.

The developed, simulated pad-dry heat dyeing process for Vat Red 1 on generic PP produced a fabric with a similar K/S value to that generated by the simulated pad-steam method at analogous pad bath formulations. Vat dyed fabrics produced by both the simulated, continuous pad-steam and pad-dry heat processes exhibited adequate fastness to wet/dry crocking, washing and dry cleaning, thus certifying them for commercial applications.

CHAPTER 1: INTRODUCTION

Since the advent of stereo-regular isotactic polypropylene (PP), the fiber has been used in many industrial applications, as well as in carpets and apparel, due to its high degree of crystallinity, good handle, strength and a high enough melting point for normal use. The potential commercial importance of unmodified polypropylene (PP) fiber in the carpet and textile industries has led to research to develop an aqueous dyeing process for the highly-hydrophobic fiber, consistent with the established coloration processes in use for other high-volume fibers (cotton, nylon, polyester and acrylic). Despite substantial research conducted around the globe, a commercially viable and sustainable aqueous dyeing process of PP based on demand-activated manufacturing has not been realized.

PP offers the advantages of exceptionally low price, good strength and aesthetic properties, along with many other desirable characteristics of a textile/carpet fiber, thus creating the impetus for manufacturing from PP fiber a variety of materials such as towels, floor coverings, sportswear and select technical products. Due to its nonpolar and hydrophobic nature, most of the production of PP fiber is colored by means of mass pigmentation. This route of coloration gives excellent fastness properties during end use; however, it restricts the producer in fulfilling the changing fashion demands of the market. An alternative way of coloring PP fiber exists in which the fiber can be made dyeable by means of post modification, creating active sites for dye association or adding hydrophilic comonomers, but this route has adverse effects on the mechanical properties and costs of the fiber. The development of a truly aqueous process for dyeing PP in its

generic, unmodified form is of significant importance vis-à-vis the rising demand for this relatively inexpensive fiber.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

2.1.1 Introduction to PP Fiber

PP fibers belong to the newest generation of large-scale, manufactured chemical fibers, having the fourth largest volume in production after polyesters, polyamides and acrylics [3,4]. PP is one of the most successful commodity fibers, reaching a world production capacity of four million tons a year. Due to its low density (0.9 gm/cc), high crystallinity, high stiffness and excellent chemical/bacterial resistance, isotactic PP is widely used in many industrial applications such as nonwovens, industrial ropes, packaging materials, furnishing products, etc. PP fiber has potential, high-volume applications in the carpet, textile, apparel and industrial textile markets.

Due to its thermoplastic nature, PP fiber is manufactured using conventional melt spinning. Subsequent multistage drawing imparts tensile strength and enhances mechanical properties required for industrial applications. Synthesis of PP polymer involves stereo-regular polymerization of propylene gas using Ziegler-Natta catalysts [5]. Only isotactic polypropylene is useful for fiber applications among the three stereoisomers. Since only a simple monomer, i.e., propylene gas, is involved in the synthesis of PP, this fiber is relatively inexpensive to produce as compared to other high volume textile fibers such as polyesters, acrylics and nylons. The major products of PP fibrous materials are monofilaments, multifilament yarns, staple fibers and yarns,

nonwoven textiles (spunbond, meltblown), tapes, split filament, ropes, carpet backing, etc. Crystallinity of isotactic PP is about 70%, and the molecular weight of fiber grade PP is in the range of 80,000 to 300,000 gm/mole.

2.1.2 Requirements of Dyeability

The basic requirements for any fiber to be aqueous dyeable are [6]:

a) The dye molecule must be able to diffuse inside the solid state structure of the fiber.
b) The fiber should possess some dye receptor sites within its polymer system to chemically interact or attach with the dye molecules in order for the colored textile to be resistant to washing, crocking and dry-cleaning. The fiber can also be colored by means of physical entrapment of the dye molecules inside of the amorphous domains of the fiber.
c) The major portion of the dye mass should transfer from the aqueous phase to the fiber phase.

The third requirement is automatically satisfied if the first two are met.

Apart from the above basic requirements, additional requirements of dyeability from a commercial point of view are:

a) The fiber should be dyeable or printable with commercially available equipment and technologies.
b) The chemicals, dyestuffs and auxiliaries should be commercially available and not overly expensive.
c) Complete or near complete exhaustion of dye baths, level dyeings, availability of a wide range of shades and adequate fastness properties are critical requirements.

2.1.3 Forces of Interaction between Dye and Fiber

The variety of binding forces occurring between dyes and fibers include [6] :

a) Chemical (ionic, covalent, coordinate)

b) Polar (hydrogen, electrostatic)

c) Nonpolar or Van der Wall's forces

Examples of the above forces include: ionic bonds between acid dyes and wool; covalent bonds between reactive dyes and cellulosic fibers; coordinate bonds between metal atoms and dye molecules in mordant dyeing; and hydrogen bonds between direct dyes and cellulosic fibers. The weakest bonds among those listed above are the nonpolar or Van der Wall's interactions that take place between disperse dyes and polyester fibers. However, disperse dyed polyester fibers exhibit excellent wash- and crock-fastness characteristics. In fact, disperse dyes are mainly held in polyester fibers via physical entrapment of the colorant molecules within the collapsed polymer chains comprising the amorphous regions.

2.2 Miscibility and Diffusion of Small Penetrant Molecules into Polymers

2.2.1 Introduction to Miscibility [7,8]

An ideal solution is defined by a system of two components which mix together, leading to a free energy change that is solely determined by the entropy gain by each component due to additional degrees of freedom coined by the solution process. This entropy gain is known as the combinatorial entropy and is given by [7]:

$$\Delta S = -k(N_1 + N_2)(x_1 \ln x_1 + x_2 \ln x_2) \quad \text{Eqn. 1}$$

Here x_1 and x_2 are the mole fractions of component i. N_1 and N_2 are the number of repeat units in polymer and solvent, respectively. For an ideal solution, the enthalpy of mixing is always zero. The components which form an ideal solution will always be completely miscible. In the case of regular solutions, the enthalpic term (nonzero) is given by [7]:

$$\Delta H = (N_1 + N_2)zwx_1x_2 \qquad \text{Eqn. 2}$$

Here z is the coordination number and w is the exchange energy. The resultant free energy of mixing for the regular solution is thus [7]:

$$\Delta G_M = (N_1 + N_2)zwx_1x_2 + kT(N_1 + N_2)(x_1 \ln x_1 + x_2 \ln x_2) \qquad \text{Eqn. 3}$$

Based on the lattice occupancy by the polymer segments, the Flory-Huggins equation for the entropy of mixing of a polymer with a solvent is [8]:

$$\Delta S = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \qquad \text{Eqn. 4}$$

Here ϕ_1 and ϕ_2 are volume fractions of polymer and solvent, respectively and χ is the Flory-Huggins interaction parameter.

For polymer solutions in which N_1 = N and N_2 = 1, the Flory-Huggins equation for the free energy of mixing is [8]:

$$\Delta G_M = kT\left[\frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right] \qquad \text{Eqn. 5}$$

The first two terms in the equation are entropic and the third term is enthalpic in origin. The entropic terms always promote mixing, although the magnitude of these terms is very small for the blends of long chain polymers. The last term is energetic and can be positive (opposing mixing), negative (promoting mixing) or zero (ideal mixtures), depending on the sign of the Flory-Huggins interaction parameter, (χ).

For non-polar mixtures in which species interact mainly via dispersion or van der Walls' forces, the interaction parameter (χ) can be calculated using the method developed by Hildebrand and Scott, which is based on the solubility parameter (δ) equal to the square root of the cohesive energy density of a molecule [8]:

$$\delta = \sqrt{\frac{\sum E_i}{\sum v_i}} \qquad \text{Eqn. 6}$$

E_i is the cohesive energy or energy of vaporization, and v_i is the molar volume of the individual atom or group of atoms present in the molecule. The individual atom and functional group contributions to E and v in a given molecule are available in Fedors' table [9].

The interaction parameter (χ) can be written in terms of the solubility parameter (δ) and the volume per site (v_0) [8]:

$$\chi = \frac{v_0}{kT}(\delta_A - \delta_B)^2 \qquad \text{Eqn. 7}$$

The temperature dependence of the interaction parameter (χ) is [8]:

$$\chi(T) = A + \frac{B}{T} \qquad \text{Eqn. 8}$$

The temperature dependent term A is known as the entropic part of the equation, while B/T is termed the enthalpic part. The main assumption of the Flory-Huggins theory is that no volume change occurs upon mixing, while in real polymer blends the volume per monomer changes slightly upon mixing.

2.2.2 *Theory of Small Molecule Diffusion into Solutions*

The trajectory of a colloidal particle in a liquid is an example of a random walk, where the particle diffuses randomly into the liquid [8,10,11]. The three-dimensional root mean square displacement of the particle during time t is proportional to time t, with the proportionality coefficient known as the diffusion coefficient, D [8]:

$$\left\langle [r(t) - r(0)]^2 \right\rangle^{1/2} = (6Dt)^{1/2} \qquad \text{Eqn. 9}$$

Here r is the position of the particle. The diffusion coefficient D and the friction coefficient (ζ) are related through the Einstein relationship [8]:

$$D = \frac{kT}{\zeta} \qquad \text{Eqn. 10}$$

where k is the Boltzmann constant and T is the absolute temperature.

The combined Stokes-Einstein relation for the diffusion coefficient of a spherical particle of radius R in a Newtonian liquid of viscosity (η) is given by [8]:

$$D = \frac{kT}{6\pi\eta R} \qquad \text{Eqn. 11}$$

Fick's second law of mass diffusion is [10,11]:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \qquad \text{Eqn. 12}$$

Here C is the concentration of the small molecule in the solution and x is the direction of the diffusion.

2.2.3 Polymer-Small Molecule Interactions

The diffusion of small molecules into a polymeric system is associated with many practical applications of industrial importance. Diffusion of gases, fillers, carriers, plasticizers, surfactants, dyes and pigments into polymeric systems are particularly of great interest due to their commercial importance. Other applications of small molecule diffusion into polymers include packaging materials, drug delivery systems, ion selective membranes and polymer coatings.[9] Diffusion governing theories of the interaction or miscibility of these small molecules into amorphous, semi-crystalline and crystalline polymers provide a strong scientific basis for the prediction of the nature of interaction as well as the degree of miscibility of these molecules with the polymers.[4] The theoretical work in this field is divided into two categories: the free volume models which focus on the statistical distribution of holes in the lattice, and the molecular dynamical models which include the nature of interaction between the small molecule and polymer.

Characterization techniques used to measure the translational diffusion coefficient in polymers include [10]:

a) Fluorescence quenching
b) Fluorescence recovery after photobleaching
c) UV/vis and infrared spectrophotometries
d) Mass uptake
e) Charge transfer techniques
f) Capillary column inverse gas chromatography
g) Molecular dynamics simulation

Morrissey et al. [12] used light microscopy without staining the penetrant by in situ video recording and computer analysis. They observed that the penetrant diffuses into the voids present in the polymer matrix and the presence of voids enhances the diffusion rates of the penetrant.

Demco et al. [13] studied the self-diffusion anisotropy of the various n-alkanes into natural rubber of different crosslink densities by using pulse gradient stimulated spin-echo NMR. They measured the diffusion coefficients and displacement probabilities of penetrant molecules along, as well as perpendicular to, the direction of the compressive force.

Boshoff et al. [14] studied helium diffusion in atactic polypropylene of various densities (0.8-0.9 gm/cc) by performing molecular dynamics simulation for both rigid chains as well as fully mobile chains. The authors selected the appropriate simulation box size and observed that the diffusion mechanism for the rigid matrix was anomalous and proceeded via a tortuous path. On the other hand, mobile matrix presents helium diffusion with the Fickian trend. The role of polymer structure in the diffusion process has been studied by the authors.

Pavel et al. [15] studied the diffusion of oxygen and carbon dioxide in various blends of bulk amorphous polyethylene terepthalate and other aromatic polyesters at different temperatures. The authors created polymers with DP = 20 using modeling of the chemical structures and subsequently performed molecular dynamics simulations to investigate the diffusion of oxygen and carbon dioxide into the simulated polymers of varying densities via measuring diffusion coefficients. The authors found that the diffusion coefficient was` completely determined by the jump event of the penetrant

molecule in the available free volume of the polymer system, as the diffusion coefficient correlated with the accessible free volume fraction in the polymer. The authors reported an exponential increase in the diffusion coefficient with the free volume. An increase in temperature increased the diffusion coefficient, while an increase in the diameter of the diffusing molecule lowered the diffusion coefficient.

Effects of dye-polymer interactions on the glass transition temperature (T_g) of the polymer after the formation of solute-polymer blend have been studied by Slark et al. [16]. In some polymers the dye caused a decrease in $T_{g,}$, whereas in others it increased the T_g of the polymer. They concluded that an elevation in T_g was indicative of higher dye-polymer affinity and hence better dye-polymer interactions, whereas depression in T_g was indicative of the plasticization of the polymer caused by the dye molecules. They also observed excellent correlation between T_g enhancement and dye-polymer solubility parameter match.

The effect of specific interactions on the dye transport in polymers has been investigated for various amorphous polymers by Slark and Hadgett [17]. The authors concluded that diffusivity is strongly affected by the polymer's T_g, whereas solubility is regulated by the balance of physical forces and particular interactions between the dye and the polymer. They established a good correlation for diffusivity as a function of polymer T_g, dye-polymer solubility parameter difference, and specific dye-polymer interaction determined by IR spectrophotometry, and concluded that maximum diffusivity will result by a combination of low T_g, match in the dye-polymer solubility parameter and strong acid-base, dye-polymer interactions.

Single molecule spectroscopy and theoretical techniques (quantum-chemical calculations and Monte Carlo and molecular dynamics simulations) have been used by Vallee et al. [18] to probe dye-polymer interactions. The authors concluded that the dye molecule adopted planar and non-planar conformations. An in-depth analysis of fluorescence lifetime trajectories revealed that the planar conformers can be further classified depending on their side chain interactions with the surrounding polystyrene chains.

2.3 Coloration of PP Fiber

2.3.1 Melt Pigmentation of PP Fiber

The major portion of colored PP fibers is currently manufactured by melt pigmentation (called spun dyed fibers)[19]. Melt pigmentation involves the addition of pigment particles in the polymer melt prior to extrusion and fiber spinning. Melt pigmentation can be performed in various ways. Pigments can be added to the pre-melted fiber polymer, or it can be mixed with the chips (also known as chip pigmentation) in order to produce melt pigmented PP fibers.

2.3.2 Different Methods to Aqueous Dye PP Fiber

Three general approaches to aqueous color PP fiber are reported in the literature [6]:

a) Attempts to color unmodified PP fiber with modified dyeing methods.

b) Modification of the fiber surface to create dye receptive sites.

c) Copolymerization and graft copolymerization.

The influence of dyestuff constitution and auxiliaries in the dyeing of unmodified PP has been studied by Herlinger et al.. The authors determined that the use of toluene and p-xylene as carriers, together with some anthraquinone disperse dyes having longer alkyl groups, improved the fixation of dyes into PP fiber by increasing the intermolecular forces between dye and fiber.

Oppermann et al. [20] reported the synthesis of disperse dyes with alkyl substituents of varying lengths and dyed unmodified PP with them at a high temperature (125^{o}C) for 150 min. Wash fastness of the dyed samples increased on increasing the chain length of the alkyl substituent; however, the levelness also decreased. An octyl substituent proved an optimum length for good fastness and levelness properties.

Stright et al. [21] reviewed different ways to dye PP including the development of new dyes which were fixed in the fiber by formation of dye-metal complexes on the metal-containing PP fiber, resulting in adequate dyeings in a variety of shades. Dye-metal complex forming dyes could be applied to a wide variety of materials utilizing standard dyeing techniques.

Reactive modification involves treatment of PP fiber with certain chemicals in controlled-conditions [6]. This type of modification increases costs in excess drying, handling, recovery of materials and operational steps. The treated fibers also showed ring dyeing and inferior physical properties. Reactive modification is thus not a commercially viable option.

Incorporating dye receptive groups in a polymer chain is known as copolymerization, whereas attaching a segment of a dye receptive group as a side

chain is termed graft copolymerization [6]. Several disadvantages are associated with the copolymerization of PP:

a) Copolymerization of PP with polar compounds gives low efficiency.
b) Polar compounds impede the crystallization behavior of PP and also decrease the melting point of the polymer.
c) Copolymerization adversely affects the physical and mechanical properties of the polymer.

Graft copolymerization was more technically appealing in the case of PP, but the expensive technology was considered as a barrier to the commercial adaptation [6].

2.3.3 Addition of Dye Receptors

Addition of dye receptor additives prior to fiber extrusion has been explored by many researchers [6]. Three different classes of these additives are:

a) Metallic compounds
b) Polymeric additives
c) Low molecular weight organic and inorganic compounds

The additive approach can be divided into four major areas of research involving the development of:

a) Disperse dyeable fiber using major disperse, vat and azoic dyes
b) Disperse dyeable fiber using mordant disperse dyes
c) Acid dyeable fiber using anionic dyes used for wool
d) Basic dyeable fiber using cationic dyes

Brown et al. [22] reported disperse and acid dyeable olefin fibers. The dyeable olefin fiber was prepared in two ways: (a) formed a blend of alpha-monoolefin polymer and 1-5% by weight of a pyridine type polymer dye receptor which led to disperse dyeable PP fiber; (b) formed a blend of less than 97% by weight of alpha-monoolefin polymer, 0.5-5% by weight of pyridine type polymer dye receptor and 0.5-5% of hydrophilic compound containing ethylene oxide units. The resultant fibers were dyeable by both anionic and disperse dyes. The approach was to dye the uniformly-dispersed additives so that the whole fiber appeared colored. This approach was found much easier and efficient than fiber pretreatments, copolymerization or grafting, and also less harmful to the fiber's physical properties.

2.3.4 Disperse Dyeable PP Fibers

The advantages of disperse dyeable PP fibers were:

a) The availability of a wide range of disperse dyes, eliminating the requirement of developing new dyes.
b) The leveling properties of disperse dyes were excellent.
c) Vat and azoic dyes could also be used after a slight modification in the process.
d) The result was excellent wash fastness due to water insolubility.

Grafting of dye enhancers to the polyolefin polymer has been reported by Negola et al. [23,24]. A mixture of amorphous PETG (glycol-modified polyethylene terephthalate) was grafted onto polyolefin. Maleic anhydride was added to increase the cohesion and dispersion of amorphous PETG in polyolefin polymer. A formulation of 50% PP, 48% amorphous PETG and 2 % maleic anhydride was used and the resultant pellets were

extruded into fiber form. A 5% disperse dyeable mixture grafted onto 95% PP resulted, which upon dyeing yielded deep shades, whereas a 2.5% disperse dyeable mixture onto 97.5% PP yielded light shades.

Addition of polymeric dye receptors has been investigated by Farber et al. [25] and Dayioglu et al. [26]. Disperse dyeable PP fiber was manufactured to be consumed in the carpet industry. The approach involved addition of selected polymeric compounds into the PP melt prior to extrusion. Certain limitations of using polar polymeric compounds exist:

a) Subsequent spinning and drawing operations become difficult because most of the polar polymeric compounds lack compatibility with PP.
b) As the polarity of admixing compounds increases, their compatibility with PP decreases. Therefore, polyamides and polyesters with strong polar groups are less compatible with PP than polystyrene and ethylene copolymers.
c) The melting point of most polar compounds is higher which requires a high processing temperature, resulting in the degradation of PP.
d) Many polymeric additives suitable for processing purposes do not have enough polarity to give adequate wet- and dry-cleaning fastness.
e) Most of the polymeric additives require amounts over 10 % to be incorporated into the PP fiber to achieve satisfactory dyeability. Large quantities of incompatible and partially-miscible additives adversely affect the physical and mechanical properties of the resulting fiber.
f) The fiber is more costly than the generic version.

In relation to the above challenges, the selection of an appropriate PP additive with all-round adequate properties becomes difficult. An ideal polymeric additive for PP should possess polar groups lying pendant to its chain, be slightly crystalline in nature, have partial compatibility with PP, have a melting point greater that 140^{o}C and have a glass transition greater than 90^{o}C. Polymers such as saturated linear copolyesters, copolyamides, copolymers of vinyl pyridines with styrene, copolymers of ethylene with vinyl acetate and alkyl acrylate may work as such ideal additives.

In conclusion, disperse dyeable PP fibers are comparatively easy to produce and result in level dyeings, although they are more expensive than the generic fiber (usually >$1.00/lb. premium). However, the fastness properties of the dyed materials do not meet all the requirements of the textile and apparel businesses, especially due to their poor dry-cleaning fastness to perchloroethlene (PERC). In addition, a similar chlorinated solvent (trichloroethylene) is commonly used as a spot cleaning agent in carpets, both in manufacturing and in residential/commercial use. The shades obtained by acid and basic dyes are also brighter than those obtained with disperse dyes.

FiberVisions recently launched CoolVisions® (a disperse dyeable PP fiber) [27] having a dye receptor as an encapsulated additive in the polymer matrix. The dye receptor additive is an amorphous, low molecular weight copolyester. A compatibilizer is finely distributed and encapsulated in the microstructure of PP [28]. The modified PP fibers are manufactures by sheath-core bicomponent spinning consisting core as dye receptor and sheath material as PP.

2.3.5 Acid Dyeable PP Fibers

The advantages of acid dyeable PP fibers include [6]:

a) Acid dyes are inexpensive, offering a wide range of shades with bright colors.

b) Light fastness is excellent.

c) In some cases, acid dyeable PP fibers also have affinity for disperse dyes.

While most of the acid dyeable PP fiber versions have failed in the development stage due to their lack of commercial viability, some of them have survived. Those which have shown commercial success include acid-dyeable PP fiber from Montecatini (Mercalon D®), Hercules (Herculon® Acid Dyeable), Beaunit, Phillips and Toyobo. Out of these, Mercalon D® was dyeable with almost all anionic dyes up to dark shades. Mercalon D® is presently available as a staple fiber for carpets and knitting yarns. Merkalon D®'s use is increasing because its dyeing profile is similar to that of wool. Merkalon D® has a leveling problem in piece dyeing because of its high affinity to acid dyes and high rate of dyeing. Apart from a few limitations and high cost per pound, Merkalon D® fiber appears to have achieved the status of a commercial, general purpose fiber in the carpet and knitting industries.

Arkman et al. [29] reported the mixing of an additive in the PP polymer prior to fiber extrusion. The additive was synthesized by attaching long alkyl chains having substituents such as alkaline nitrogen to a rigid polymer backbone. They found a diffusion coefficient of dyeing in the order of 10^{-11} m^2/s, which indicated very fast diffusion of the acid dye molecules into the modified fiber driven mainly by the electrostatic interaction between the anionic acid dye and basic dye sites in the polymer contributed by the additive.

The use of Koprolene colors (dyes having a metal chelating group) for modified PP fibers containing nickel salt stabilizer has been reported by Baumann et al., [30] and has demonstrated attractive shades with excellent fastness properties to washing, dry-cleaning, crocking, light and gas fading. The scoured yarn or fabric was recommended to be dyed at 190 to 200^{o}F for one hour and finally to be washed.

2.3.6 Dyeing Mechanism of PP Fibers

Since none of the commercially-dyeable PP fiber was available long enough to explore its dyeing behavior [6], only a few scattered studies were reported. The dyeing of hydrophobic fibers with disperse dyes takes place through the solid solution mechanism, i.e., the dye forms a solution within the amorphous region of the polymer. The dye mass transfer from dyebath to the fiber phase is governed by the partition coefficient of the dye. Bird and Patel [31] have shown that the introduction of additional dye into the dye bath beyond the saturation point of the fiber phase did not increase the amount of dye inside the fiber.

Since generic, isotactic PP fiber has only ~30% amorphous mass accessible to dye molecules, the saturation value is low. The encapsulation of a suitable dye receptor additive into the PP matrix causes the amorphous regions of the fiber to increase, leading to the availability of more solvent for the dye to form a solid solution, and thus increasing the saturation values of the fiber. However, the physical properties of the PP fiber, e.g., the percent crystallinity, are lowered when additives are occluded in the solid state structure, and since the cost of the fiber is also increased, both factors detract from use of the modified fiber in textile/carpet products.

2.3.7 Dyeing of Unmodified PP

Calogero et al. [32] reported dyeing of unmodified PP fibers using a colloidal emulsion of water plus long-chain, alkyl-substituted anthraquinone dyes dissolved in an organic solvent. Alkyl chains with carbon numbers from 8-18 were described, and the 18 chain length was found as ideal for PP. The ideal dyebath temperature was reported as 90^{o}C. The dyeing resulted in uniform coloration of the PP fibers with excellent fastness to washing, crocking and dry-cleaning.

Vat dyes captured a large part of the dyestuff market in the coloration of cellulosic fibers because they provide excellent all-round fastness, particularly to light, washing and chlorine bleach. Because of their insoluble nature in the oxidized form, vat dyes require a complicated application procedure involving the reduction of the oxidized form into first the leuco form and then with base into the more water-soluble alkaline leuco form. The soluble, reduced alkaline leuco form has high substantivity towards cellulosic fibers, and after levelness is achieved, the dyes are re-oxidized into the original, water-insoluble keto form inside the fibers.

Sodium dithionite and sodium hydroxide produce large amounts of sodium thiosulfate and sulfites as a byproduct, increasing the cost of effluent treatment. Ressler et al. [33] reported electrochemical methods for reduction of vat dyes which are environmentally friendly, thus providing an alternative to the use of sodium dithionite and sodium hydroxide.

A. V. Mishchenko et al. [34] investigated the batch exhaust dyeing of staple PP fiber at 100^{o}C and 80^{o}C with the acid leuco vat dyes thioindigo red S, thioindigo reddish brown Zh and thioindigo red S (actual chemical structures were not revealed). They

plotted a dye exhaustion curve as shown in Figure 2.1 (dye adsorption versus dyeing time) and calculated the heat of dyeing and entropy of dyeing. The heat of dyeing was observed as negative, indicating the strong interaction between the acid leuco vat dye and the PP fiber. The measured heat of dyeing of acid leuco vat dye on unmodified PP was of the same order as that in the disperse dyeing of PP fiber

The authors also investigated the effect of heat treatment [35]on the fixation of acid leuco dyes on PP fiber. The process sequence involved padding of PP fiber with the acid leuco vat dye solution, squeezing, drying and then treating with dry heat for 1 to 10 minutes. The authors noted that the heat treated fibers resulted in better fastness properties, and thus demonstrated that the heat treatment helped in the fixation of dye molecules via diffusion. The rate of dyeing increased on subsequent heat treatment (Figures 2.1-2.2).

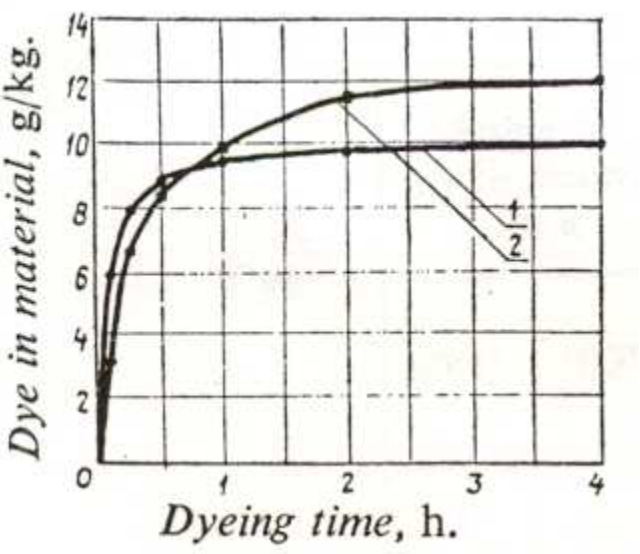


Figure 2.1. Dyeing Rate Curve of the Leuco Acid Form of Thioindigo Red S on PP Fiber: (1) at 100°C; (2) at 80°C [34]

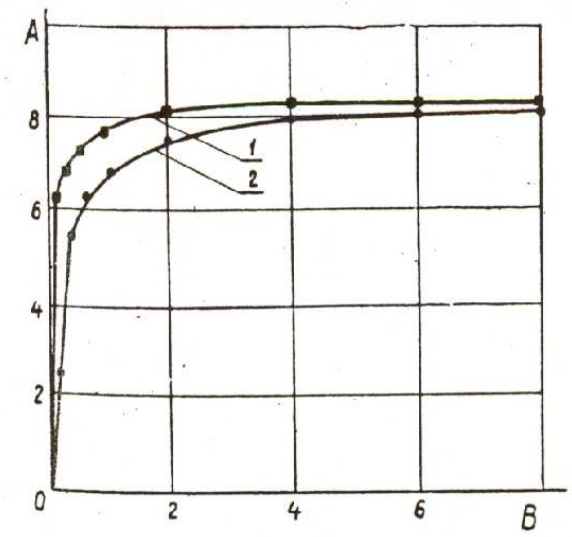


Figure 2.2. Exhaustion Curves of Vat Red 2 on PP Fiber; 1- with Subsequent Heat Treatment, 2- without Heat Treatment. A-axis: Exhaustion, B-axis: Dyeing Time [35]

Morozova et al. [36,37] investigated the process of developing the leuco esters of vat dyes on PP fiber by a nitrite method and optimized the development conditions for maximum color yield:

Temperature: 60°C; development time: 40 min.; liquor ratio: 50; liquor composition: 12.5% H_2SO_4, 2.2 g/l $NaNO_2$. The authors obtained satisfactory light and weathering fastness for the PP dyed with leuco-ester of Vat Brilliant Green S [37].

Bird and Patel [31] studied the dyeing of unmodified PP yarn and film with disperse dyes and concluded that no fundamental difference existed between PP and other substrates in the diffusion mechanism. Figure 2.3 showed the Nernst isotherm partition mechanism of dye adsorption between fiber and aqueous phase, which was similar to that

followed in the disperse dyeing of polyester fiber. Figure 2.4 exhibited the rate of dyeing curve for disperse dye on generic PP, indicating that the rate of dyeing increased with increasing dyeing temperature.

Unmodified PP is more crystalline, nonpolar and hydrophobic than other synthetic fibers [31]. Moreover, the absence of hydrogen bonding groups in PP also precludes the fiber from attaching to the diffused dye molecules, resulting in the poor saturation values. Further, diffusion coefficients of disperse dyes in PP were higher than in cellulose acetate fibers, indicating that diffusion of the dyes inside the PP fiber was not the reason of poor saturation. Weak intermolecular interactions between disperse dyes and PP were concluded to be the reason for the poor saturation values.

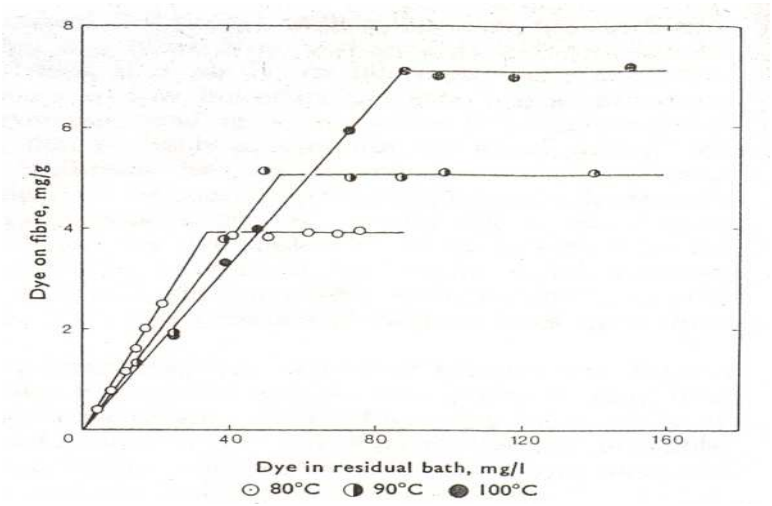


Figure 2.3. Adsorption Isotherms for Dimethyl Yellow on Unmodified PP at various Temperatures [31]

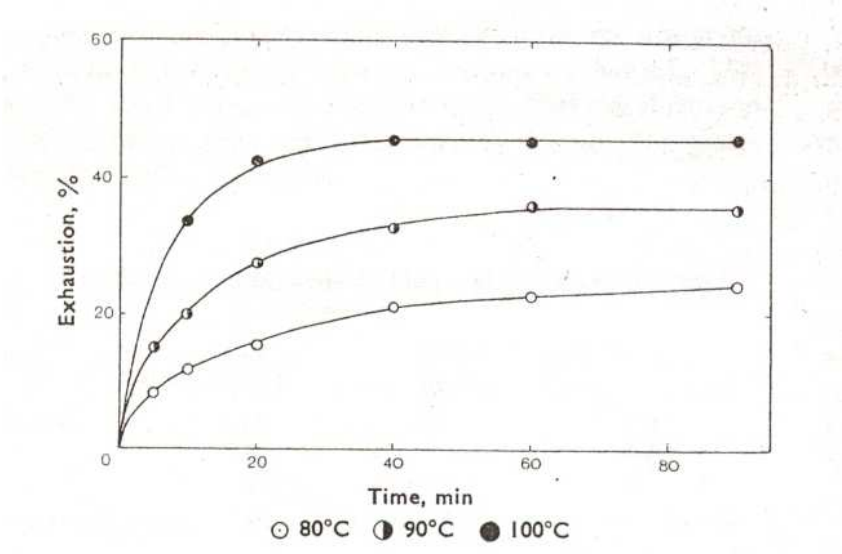


Figure 2.4. Dyeing Rate Curve for Serisol Fast Pink RGL Disperse Dye on Unmodified PP [31]

According to Ulrich et al. [38], vat dyes when applied in their oxidized or vat acid forms in a colloidal state of dispersion under proper temperature conditions diffuse into highly hydrophobic fibers. Three methods of vat dye application on unmodified polypropylene fibers were employed: Exhaustion, pad-steaming and printing with steam fixation:

Conditions for Exhaustion Method:

Temperature: 120-135^{o}C, preferably 130^{o}C

Time: 40-70 minutes, preferably 60 minutes

Dispersion system recommended for exhaustion method:

Non-ionic auxiliary based on alkyl or alkylaryl-polyglycol ethers or oxethylated fatty acid polyglycol esters, e.g., a reaction product of 1 mole isotridecyl alcohol and 8 moles of ethylene oxide.

In addition to the above auxiliary, the exhaustion method dispersion system also consisted of an anionic protective colloid having a dispersing effect based on lignin sulfonic acid. Optionally sodium sulfate was used as an electrolyte in the exhaustion method.

Pad Steaming /Print Steaming Method:

Temperature: 100-135^{o}C, preferably 130^{o}C

Time: 10-40 minutes, preferably 30 minutes

Non-ionic protective colloid having a thickening effect based on completely etherified locust bean flour is used.

Under high temperature conditions, reducing agents lost efficiency and the dye was dispersed under the influence of a dispersing agent. In the vat acid method, the dye already was in the dispersed form. Leuco esters of vat dyes were solubilized vat dyes prepared by reacting vat dyes with a chlorosulfonic acid, and when they reacted with acetic acid, they adopted the form of the vat acid.

Solvent Method:

Vat dye and dimethyl formamide (1:3 to 1:10) were added to water with continuous stirring and, a protective colloid (based on lignin sulfonic acid) was also added while stirring; a fine pigment dispersion resulted. The color yield was less in this case than that of the aqueous method.

The vat dyes used by the authors were (Table 2.1):

Table 2.1. Vat Dyes with C. I. Number Used by Ulrich et al. [38] to Dye Unmodified PP

C. I. Name of Vat Dye	C. I. Number
Vat Yellow 29	68400
Vat Orange 7	71105
Vat Red 14	71110
Vat Red 15	71100
Vat Blue 4	69800
Vat Green 1	59825
Solubilized Vat Green 21	59051

Vat Acid Method:

After vatting, the acidification was accomplished with a sodium hydrosulfite solution (40 ^{o} Be) to obtain the vat acid form of the dye.

Steam Padding Method:

PP fabric was padded with vat dye, completely etherified locust bean flour and a non-ionic dispersing agent and then dried. After that, the material was cross padded with a reduction agent based on sulfonic acid derivative, sodium hydroxide and sodium sulfate and then steamed at 130^{o}C for 30 minutes. Finally, batching, rinsing and re-oxidation steps were carried out.

Most of the processes used by the authors yielded dyeings with brilliant colors and very good fastness properties.

Burkinshaw et al. [39] investigated dyeing of textile fibers including: segmented polyurethanes, segmented polyurethane ureas and segmented polyetheresters; polyesters

including poly(tetramethylene terepthalate); polyamides including poly(hexamethylene adipamide); and polycaprolactam with acid leuco vat dyes utilizing alpha-hydroxyalkylsufinic acids, their salts and 1, 2, 4-trithiolane as additional reducing agents. The authors reported excellent depth of shade and wash fastness for the dyed materials.

Etters et al. [40] reported that several vat dyes in their acid leuco form exhibited substantivity to unmodified, knitted PP fabrics with C. I. Vat Blue 1, Vat Orange 1 and Vat Yellow 2. Lu, Etters et al. [41] reported that several vat dyes (C.I. Vat Red 1, Vat Yellow 4 and Vat Green 1) in their acid leuco form (obtained by vatting the dye pastes with NaOH and $Na_2S_2O_4$ and subsequently back titrating with acetic acid to pH 7) resulted in good substantivity towards the PP fabrics. The authors plotted CIE (Commission Internationale de l'Eclairage) color parameters L* (lightness), a* (red, greenness) and b* (yellow, blueness) vs. %owf (on weight of fabric) of dye.

Gaehr et al. [42] reported that several Colloisol® vat dyes of BASF exhibited good affinity on plasma-pretreated PP fiber in a pigment pad-thermofix process at 120^{o}C. The fixation of pigments was performed in a pad-steam or pad-dry heat process, and the processes were reported to be applicable for dyeing of fiber mixtures containing PP.

2.4 Literature Review Summary and Scope of the Project

From the literature review, the substantial volume of work conducted by researchers of different laboratories world-wide confirmed that the aqueous dyeing of generic, unmodified PP fiber is of significant importance for textile, carpet, apparel, sportswear and a variety of other product applications. Most of the work carried out by researchers included the modification of PP fiber in some form or another, paths which although they impart dyeability, increase the total fiber costs two to three times above that of generic PP because of utilization of a variety of modifying chemicals, additives, comonomers or components. Another disadvantage of the fiber modification route is that it adversely affects the mechanical and physical properties of the fiber. The low cost and good physical/aesthetic properties, the two basic motivations for utilizing generic PP fiber in textiles and carpets, have been outweighed by the disadvantages and limitations of modifying the fiber solely to impart aqueous dyeability.

The primary purpose of the aqueous dyeing of PP fiber in its generic, unmodified form is to exploit the advantages this fiber offers to the market place and, at the same time, create new product markets for this inexpensive fiber in high volume consumption areas such as tufted carpets, towels, apparel, sportswear and technical textiles. These product markets are governed today by demand-activated manufacturing, and hence can only be realized by developing flexible, aqueous batch and continuous dyeing processes for generic PP consistent with commercially-established coloration technologies already in use for other high-volume, commodity fibers.

CHAPTER 3: OBJECTIVES

The main objectives of this research project are:

- To screen viable candidates of commercially available vat dyes utilizing solubility parameter and molecular dynamics simulation approaches.
- To develop optimized batch and continuous aqueous dyeing processes to color flat, woven PP fabric with an identified trichromatic series of vat dyes covering the visible spectrum from 400 to 700 nm (yellow, red and blue) plus an orange to cover the majority of shade color space.
- To evaluate the fastness properties (washing, crocking and dry-cleaning) of the dyed fabrics in order to certify the developed dyeing processes.
- To prepare rate plots and adsorption isotherms for the screened dye candidates in order to elucidate kinetics and the transport mechanism for single colorants in exhaust batch dyeings.
- To prepare K/S plots of the dyed PP fabric samples.
- To prepare dyeing rate plots for combination batch dyeings with all four colorants in the identified trichromatic series plus orange in light, medium and dark shades.
- To determine the effect of the optimized batch dyeing process on the physical properties (degree of crystallinity, tensile strength and modulus) of the dyed PP fiber.
- To develop the optimized continuous dyeing process for PP flat fabrics/carpets using simulated dyepad-dry-chempad-steam route.

- To develop the optimized, pad-dry heat (modified Thermosol®) method to continuous dye PP fabrics using a simulated vat acid pad-dry heat (130^{o}C) route.
- To evaluate K/S values and fastness properties of the simulated continuous dyed fabrics.

CHAPTER 4: TECHNICAL APPROACH

The coloration of cellulosic fibers with vat dyes is well established [43]. However, hydrophobic fibers such as PP are not dyeable by the conventional, aqueous-based methods which are successful for cellulosic fibers in which the alkaline leuco, dianion form (completely water soluble) of vat dyes is utilized. Theoretically, acid leuco vat dyeing analogous to the disperse dyeing of polyester fiber may provide a method to aqueous color unmodified PP fiber. Etters et al. [40] among others [34,35,38] reported the acid leuco vat dye route as a potential path to aqueous dyed PP fiber in its unmodified form.

Recently, researchers [44,45] investigated the process of dyeing polyester with indigo vat dye utilizing the non-ionic, acid leuco form of indigo (sparingly water soluble) to dye polyester fabrics and obtained good fastness results by optimizing the concentration of sodium hydroxide and sodium hydrosulphite. The authors noted that using excess sodium dithionite eliminated the need to back-titrate with acetic acid to achieve the acid leuco form of the vat dye [44].

The correlation between dye exhaustion and the solubility parameter for PLA fiber and disperse dyes has been reported by Karst et al. [1,2] , who showed that the closer the solubility parameter of the dye was to the fiber, the better the exhaustion of the dye. Solubility parameter (SP) is the square root of the cohesive energy density. SP of the PP and commercially available vat dyes were calculated using the Fedors group contribution method [9]. Dyes having SP values closest to that of PP were given priority in this research. Calibration curves for each dye were prepared using UV/Vis NIR Spectrophotometry.

The single stage, acid leuco vat dyeing process was utilized to dye the PP flat fabric. Various mixing parameters (Flory-Huggins interaction parameter and free energy of mixing) were predicted using Accelrys' Materials Studio® software. Dyes having the least free energy of mixing with PP were given priority in the experiments.

Exhaust batch dyeing experiments were conducted on a single bath Roaches Colortec® High Temperature Dyeing Machine at Georgia Tech, as well as on a Roaches Pyrotec Multi-Beaker Dyeing Machine at the University of Georgia, utilizing the optimized, single stage acid leuco dyeing procedure. Percent exhaustion was measured to evaluate the efficacy of each dye.

Dyed fabrics were evaluated for various fastness properties (washing, crocking and dry-cleaning) in order to certify the viable vat dye candidates. The impact of the dyeing process on the solid state structure of PP was investigated using X-ray diffraction and tensile testing. Rate of dyeing plots were prepared for the single dyeings as well as for combination dyeings. Adsorption isotherms were prepared to calculate the thermodynamic parameters of dyeing for single colorants. The K/S values of the dyed samples were determined.

In order to perform the continuous steam-pad dyeing, the PP fabric was dipped and squeezed into the solutions 2-3 times to perform the padding operations using dye pad and chempad formulations. The developed, optimized pad-steam process sequence for simulated continuous pad/steam coloration of unmodified PP fabric with acid leuco vat dyes was based upon the method first described by Ulrich et al. [38] The fabric was padded into the dye pad formulation, dried in a convection oven, padded with the

chempad formulation, steam-fixed in the lab box steamer and finally cold-rinsed, soaped, washed and air-dried.

The simulated continuous pad-dry heat process was based on the diffusion of acid leuco vat dye molecules into the swollen amorphous regions of the PP fiber at a temperature of 130^{o}C. The PP fabric was padded into the vat acid formulation, the excess squeezed out by hand, and the saturated fabric placed into a forced convection oven at 130^{o}C for 10 minutes.

CHAPTER 5: SIMULATION STUDIES TO PREDICT THE DYEABILITY OF ACID LEUCO VAT DYES ON UNMODIFIED PP FABRIC

The dye molecules were first sketched using the sketching tool of Accelrys' Materials Studio® Software. The isotactic PP polymer chain was constructed with the polymer build feature of the software with an adequate degree of polymerization. With the help of the "Blends Analysis" feature of the software, the following settings were created before running the simulation:

1. Before running the blends mixing simulations each of the dye molecules as well as the polymer molecule were run for the "Geometry-Optimization" using "Forcite" feature of the "modules" toolbar. The "forcefield" was "drieding" and the "charges" to "charge using QEQ" were selected. Only the Geometry-Optimized structures of dyes and PP were used as input structures in the blends-mixing simulations.
2. On the "modules" toolbar [46], on the "blends" button, the calculation tab was selected. From the "input" section of the "setup" tab, empty molecule cell was entered for isotactic PP as a "base" molecule, and all the vat dyes were entered one by one as "screen" molecule. The task was set as "mixing", on the "more…" button, on the display of the "blends mixing" dialog's "setup" tab; the "quality" was entered as "medium". "Return lowest energy frames" was checked and the number was kept at "50". On the "blends calculation" dialog on the "energy" tab, "forcefield" was set as "Drieding" and the "Charges" to "charge using QEq".

3. Finally, job control options were set by pressing the “Job Control” tab and selecting “My Computer” as the “Gateway location”. On the “more…” button, “Update structure” was checked and was set to “Update every 2 seconds”. Finally, the “run” button was pressed to run the simulation. The simulation took several minutes to display the mixing parameters.

CHAPTER 6: EXPERIMENTAL

6.1 Materials and Equipment

PP fabric made from spun, double ply PP yarns was obtained from TestFabrics, Inc., of West Pittston, PA, with the construction parameters:

Weave: plain

Ends per inch: 24

Picks per inch: 32

Warp count: 7.5s English cotton system

Weft count: 9.1s English cotton system

Dyes:

Dyes provided by Springs Industries, Classic Dyestuffs, Mount Vernon Mills and C.H. Patrick Company included:

Table 6.1. Selected Dyes for the Single Stage, Acid Leuco Vat Dyeing of Unmodified PP Fabric

C. I. Name of Dye	C. I. Constitution Number
Vat Orange 1	59105
Vat Green 1	59825
Vat Blue 6	69825
Vat Brown 1	70800
Vat Blue 1 (Indigo)	73000
Vat Red 1	73360
Vat Yellow 2	67300
Vat Blue 4	69800

Auxiliary chemicals:

NaOH: Laboratory grade, supplied by Fisher Scientific

$Na_2S_2O_4$: Laboratory grade, supplied by J. T. Baker

Rexan LFDD: Nonionic leveling agent, provided by Dexter Chemical LLC

Barapon C 108: Anionic chelating agent, provided by Dexter Chemical LLC

AATCC Standard Detergent 1993: supplied by AATCC

Equipment:

Roaches Colortec Dyeing Machine: Roaches International Limited, UK (Georgia Tech)

Roaches Pyrotec Dyeing Machine: Roaches International Limited, UK (the University of Georgia)

UV/Vis NIR Spectrophotometer: Cary 5G Varian

Reflectance Spectrophotometer: Hunterlab Ultrascan XE

Electronic Crock Meter: SDL Company

Tensile Tester: Instron

X-Ray Diffractometer: Rigaku

Forced Convection Laboratory Oven: Fisher Scientific

Lab Box Steamer

6.2 Calculation of Solubility Parameter for Commercially-Available Vat Dyes

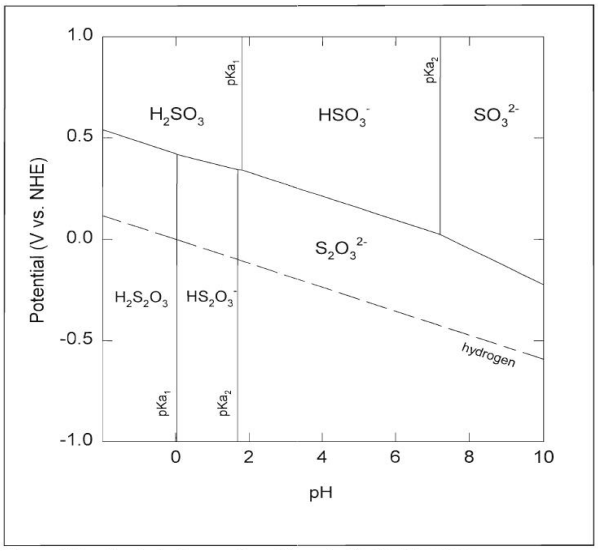
Calculation of the solubility parameter was performed using the Fedors group contribution method:

$$\delta = \sqrt{\frac{\sum E_i}{\sum v_i}} \qquad \text{Eqn. 13}$$

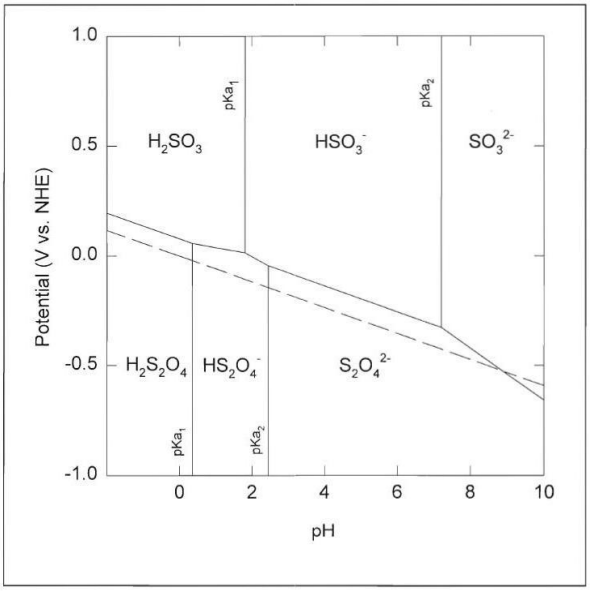
E_i is the cohesive energy or energy of vaporization and v_i is the molar volume of the individual atom or group of atoms present in the molecule.

6.3 Dyeing of Unmodified PP Using Single Stage Acid Leuco Dyeing Method with Targeted Vat Dyes

The Pourbaix diagrams (Figure 6.1) from the Scott thesis [47] show the reduction of sulfites into thiosulfate and hydrosulfite:



(a)



(b)

Figure 6.1. Pourbaix Diagrams: (a) for Sulfite Reduction to Thiosulfate; (b) for Sulfite Reduction to Hydrosulfite [47]

The potential for the former type of reduction (Figure 6.1a) is almost 400 mV more than the latter type of reduction, indicating that sulfite reduction into thiosulfate is thermodynamically more favorable. The hydrosulfite is thus relatively less stable in water as compared to an alkaline medium, solidifying the requirement to add NaOH to the dyebath prior to the addition of hydrosulfite.

The formation of the acid leuco form of vat dyes can take place in two ways:

The two-stage process of Etters et al. [41]: Vatting using sodium hydroxide and sodium dithionite and then back-titrating with acetic acid to achieve a final pH of 7;

Developed single-stage process [48]: Vatting using the least amount of sodium hydroxide and an excess amount of sodium dithionite for direct generation of a pH of 7. Indication of the formation of acid leuco compound was the visual assessment of the color of acid leuco formation of Vat Green 1 dye by both the single-stage and two-stage methods [41]. The characteristic purple-red color of the Vat Green 1 acid leuco form achieved with both the single-stage and two-stage processes confirmed that the single-stage method indeed yielded the acid leuco compound (Figure 6.2):

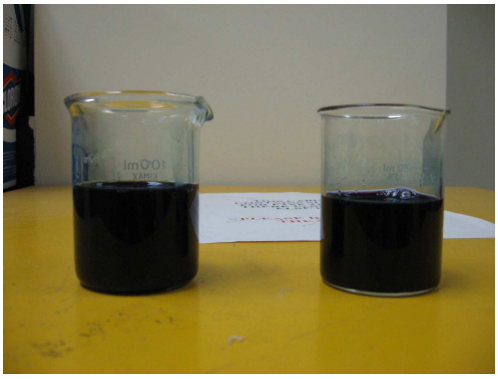


Figure 6.2. The Characteristic Purple-Red Color of the Acid Leuco Compound of Vat Green 1 Formed by the Single Stage Method (Left) and the Two Stage Acid Leuco Method (Right)

6.4 Conditions for Single Stage Dyeing Method Based on the Non-Ionic, Reduced Form of Vat Dye (Acid Leuco):

The one-position Roaches Colortec Lab Dyeing Machine (Figure 6.3) was used to dye the generic PP woven fabric.

Figure 6.3. Roaches Colortec One Position Dyeing Machine used to Dye Unmodified PP Fabric

A seventeen gram fabric sample was wrapped around the perforated sample holder of the machine after wetting with water (4-5 layers of material). The optimized, single-stage acid leuco vat dyeing cycle is shown in Figure 6.4:

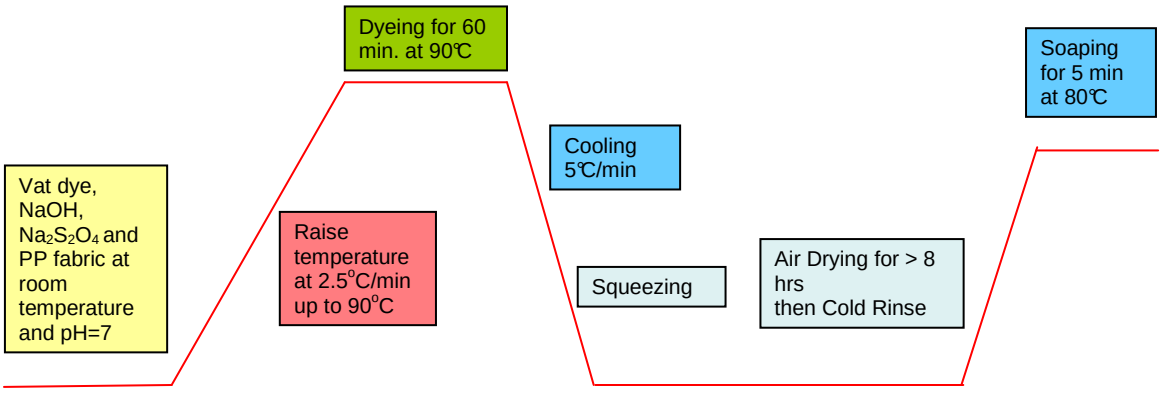


Figure 6.4. Optimized, Single-Stage Acid Leuco Vat Dyeing Cycle for Unmodified PP Fabric [48]

The optimized dyeing conditions were:

Fabric weight: 17 gms

Machine: Roaches Colortec Dyeing Machine

Sodium hydroxide: 0.8 g/l (with respect to the total dye liquor)

Sodium hydrosulfite: 16 g/l (with respect to the total dye liquor)

pH: 7

Barapon C108 (anionic chelating agent): 100 cc of 10 g/l

Rexan LFDD (nonionic leveling agent): 1.0 g/l

Liquor ratio: 100:1

Time: 60 minutes

Temperature: 90^{o}C

Oxidation: Air oxidation for 12 hours was conducted before the cold rinse step.

Soaping Conditions:

AATCC 1993 standard detergent: 5 g/l

Temperature: 80^{o}C

Time: 5 minutes

6.5 Measurement of Percent Exhaustion Using UV/VIS Spectrophotometry

In preparing calibration curves [49]:

- First 0.1 gm of dye was weighed and diluted with water to make a one liter solution (100 ppm)
- Scanning of a 50 ppm solution from 400 nm to 700 nm wavelength in the UV/Vis spectrophotometer was performed to determine the wavelength of maximum

absorption (λ_{max}). Each time a cuvette filled with distilled water was taken as a reference to the dye solution.

- A 100 ppm dye solution was diluted to 50 ppm, 40 ppm, 20 ppm, 10 ppm and 5 ppm, and each of these concentrations was measured for absorbance at (λ_{max}).
- Values of absorbance versus concentration (ppm) were plotted, and by using the regression equations determined from the plots along with measured absorbances at dye cycle time t, the dye concentrations of extracted aliquots of baths were determined.

Percent exhaustion was calculated by [49]:

$$\% \text{ Exhaustion} = \frac{C_o - C_t}{C_o} \times 100 \qquad \text{Eqn. 14}$$

C_o was the initial concentration of the dye in the bath in ppm, and C_t was the reduced concentration of the dye at time t.

6.6 Plotting Equilibrium Exhaustion Curves

The steps to prepare exhaustion curves were [49]:

- Before adding fabric into the dye bath, a 1 ml aliquot was taken to measure absorbance, and the time was designated as t = 0.
- Further aliquots were taken after the addition of fabric into the dye bath at times t = 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90 minutes.
- Percent exhaustion at each time was determined using the percent exhaustion equation (Eqn. 14).

- Percent exhaustion versus dyeing time was plotted to determine several kinetic parameters such as the half-time of dyeing, diffusion coefficient, entropy of dyeing and heat of dyeing.

6.7 Plotting Adsorption Isotherms

The fabric samples were colored using the optimized, single-stage acid leuco dyeing method on the Roaches Pyrotec Multibeaker Dyeing Machine located at the University of Georgia:

- Dye amounts in %owf (on weight of fabric): 2%, 4%, 8%, 12%, 16%, 20% and 24%.
- Measurement of percent exhaustion was performed using the UV/Vis spectrophotometer as described in Section 6.5.
- Calculation of amount of dye on fiber was made using the following equation:

$$\text{Dye on fiber} = \%\,\text{Exhaustion} \times \text{Initial amount of dye in dyebath} \quad \text{Eqn. 15}$$

- The adsorption isotherm plot of concentration of dye on fiber versus concentration of dye in solution was then prepared.

6.8 Measurement of CIE L*, a* and b* and K/S Values for Vat Dyed PP Fabrics

The Hunterlab Reflectometer Ultrascan XE sensor was standardized using the light trap/standard white tile, and was tested for accuracy before measurements using the diagnostic green tile. The green tile was scanned and the measured X, Y, Z tristimulus values were compared with the printed values of X, Y, Z of the green tile; if a close match in the printed and measured values existed, the instrument was working accurately.

D65 as standard illuminant and 10^{o} as standard observer were selected for all the measurements. After the standardization, CIE L*, a* and b* and K/S values were measured for the dyed samples. Five readings were recorded at different points on each of the dyed PP fabrics, and an average of five readings was compiled to calculate K/S for each fabric.

6.9 Evaluation of Crock Fastness: AATCC Standard Test Method 8-2004

Crock fastness was evaluated using the SDL Electronic Crock Meter by following AATCC Standard Test Method 8-2004 [50]. Dyed specimens taken for this measurement were at least 2"x5" in dimension. A white test cloth square was mounted on the rubbing finger of the instrument by firmly clamping it with the rubber ring. The dyed test specimen was clamped on the bottom fixed plate with the help of gripping pins located at the boundaries of the base plate. A standard weight was placed over the rubbing finger, and the whole upper portion, including the rubbing finger, was brought in contact with the dyed specimen. The upper arm of the instrument was lifted off after completing ten crocking cycles, and the test cloth square was removed. The rubbed area on the test specimen was marked with a pencil. Finally, the test sample was removed from the crock meter for subsequent evaluation.

Wet crocking was performed in a similar way except that the test cloth square was uniformly wetted with a drop of water before clamping it onto the rubbing finger. Evaluation of the crock fastness rating was performed using AATCC grey scales for staining on the scale of 1 to 5 (Figure 6.5). A rating of '5' was assigned to the sample

which exhibited negligible color fading or negligible staining on the white test cloth square.

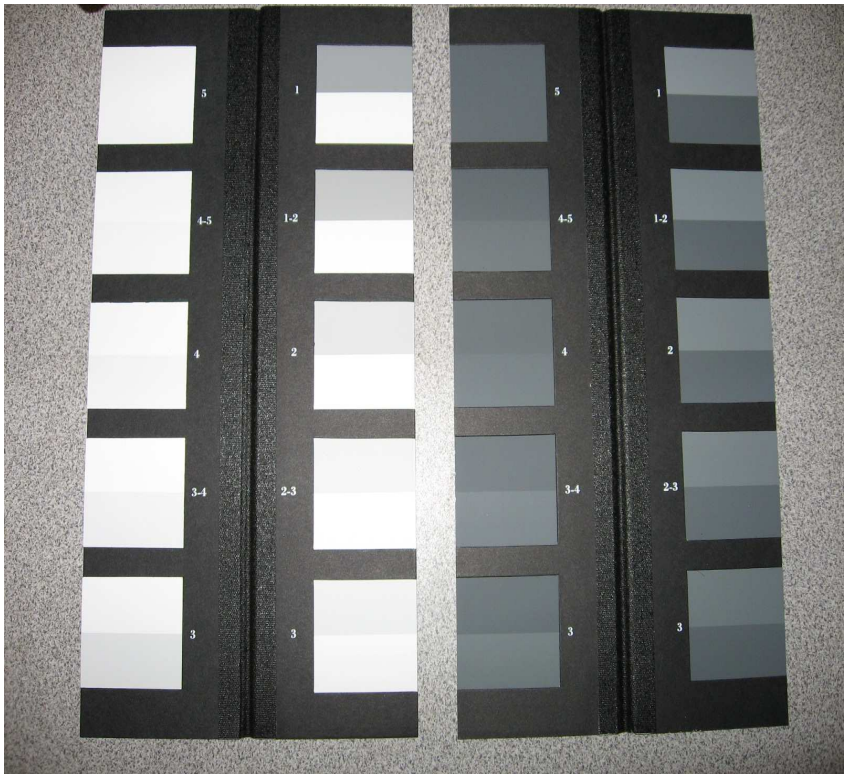


Figure 6.5. AATCC Grey Scales for Staining (Left) and for Change in Color (Right)

6.10 Evaluation of Wash Fastness: AATCC Standard Test Method 61-2003

Test II A was utilized to evaluate the wash fastness of dyed fabrics expected to undergo repeated low temperature machine washing in the home or in a commercial laundry [51]. The test conditions to perform this test were:

Temperature: 49^{o}C

Total liquor volume: 150 cc

% Detergent on total liquor volume: 0.2

Time: 45 minutes

The test specimen of 2"x5" was sewn together with the multifiber fabric strip of style # 10 and entered into the glass beaker containing the above solution and the temperature was maintained at 49^{o}C using a thermostat-controlled hot plate. The beakers were covered with the round glass plates to minimize the evaporation of the solution. Stirring was accomplished by a magnetic stirrer. After the soaping treatment, the composite specimen was removed from the beaker and rinsed twice with fresh water, squeezed and finally air dried overnight on the bench. After drying, the specimen was evaluated for wash fastness rating using the grey scale of 1 to 5.

6.11 Evaluation of Color Fastness to Dry-Cleaning: AATCC Test Method 132-2004

The entire test procedure was conducted inside of a hood. Perchloroethylene (PERC) and detergent mixtures (1% charge/volume at 75 % relative humidity) were prepared [52] using 100 ml of PERC, one drop of water and 1 gm of Perk Sheen 324 (detergent for PERC system supplied by ADCO Inc.) while stirring the contents of the

beaker. A 2”x6” specimen was taken and sewn together with the mutifiber fabric strip and placed into a beaker containing 100 cc of 1% charge of PERC-detergent mixture together with a magnetic stirrer. The beakers were kept over a thermostat-controlled hot plate, and the temperature of the hot plate was maintained at 30 ±2^{o}C for 45 minutes. The beakers were covered with round glass plates to minimize the evaporation of the solution. After the treatment, the beakers were removed from the hot plate. The samples were removed from the beakers and placed on a paper towel in a closed hood overnight (>8 hours) to dry. The remaining PERC-detergent solution was placed in a separate closed bottle and labeled as “hazardous waste”. After drying, the samples were taken out of the hood, and the fastness ratings were determined using the grey-scales for staining on the various components of the multifiber fabric and changes in color of the dyed fabrics.

6.12 Evaluation of Tensile Strength (ASTM: D 2256-97)

Influences of the dyeing process on the tensile strengths of yarns extracted from the greige (standard) and dyed fabrics were determined. Single strand yarn specimens were broken on an Instron Model 5567 tensile tester at a constant rate of elongation (60 mm/minute), and the breaking strength and the elongation at break were determined for both undyed and dyed samples [53].

The straight configuration was used in these experiments in which the yarn was clamped into the bottom clamp. After setting up a gage length of 100 mm, the other end of the yarn was clamped into the top clamp. Testing was carried out in standard atmosphere conditions (21 ± 1 ^{o}C, 65 ± 2 % RH).

Ten observations were taken for each dyed fabric sample and an average was considered for the comparison to the undyed sample. Breaking tenacity was calculated by:

$$B = \frac{F}{T} \qquad \text{Eqn. 16}$$

B= breaking tenacity in gm/denier

F= breaking force in gm

T= linear density of yarn in denier

Tensile modulus was determined using:

$$\text{Tensile modulus} = \frac{\text{Breaking stress}}{\text{Breaking elongation}} \qquad \text{Eqn. 17}$$

6.13 Degree of Crystallinity of Dyed PP Fibers

Another important solid state structure parameter for a fiber is the degree of crystallinity. The impact of the dyeing process on crystallinity was investigated by measuring wide angle X-ray diffraction patterns of undyed and dyed PP fabrics. The area under the peak was determined in the intensity versus 2θ plots. The equation to determine the degree of crystallinity (X_c) was:

$$X_c = \frac{\text{Area under the crystalline portion of the peak}}{\text{Total area of the peak}} \qquad \text{Eqn. 18}$$

The background intensity (amorphous intensity) was subtracted from the I(s) versus 2θ plot in order to separate the area of the crystalline peak from the total peak area. The integral form of Eqn. 18 was:

$$X_c = \frac{\int_0^\infty s^2 I_c(s)ds}{\int_0^\infty s^2 I(s)ds} \qquad \text{Eqn. 19}$$

6.14 Continuous Pad-Steam Simulation Dyeing of Unmodified PP Fabrics

Continuous dyeing processes are commercially well-established, particularly in the carpet and flat woven fabric/towel manufacturing industries. Continuous dyeing allows minimum production time and efficient usage of raw materials and manpower compared to batch dyeing. Vat dyes are currently utilized to color cotton fiber in pad-steam fixation processes in the flat fabric/towel industry, portending the development of an analogous dyeing process for generic PP products [43]. Similarly, the volume dyeing production process in use today for tufted nylon carpet coloration is continuous pad/steam acid dyeing. Future generic PP carpets will therefore need to be processed in a similar manner.

The PP fabrics were dipped and squeezed into the solutions 2-3 times to perform the padding operations using dye pad and chempad formulations. The developed, optimized process for simulated, continuous pad/steam coloration of unmodified PP fabric with acid leuco vat dyes was based upon the method first described by Ulrich et al.[38]:

Fabric weight: 20 gms

Dye pad:

Amount of dye: 5.7 gm (based on 70% wet pickup and 8% owf)

Albaflow pad 01 (wetting agent of Huntsman Chemical Company): 6 cc of 1% solution (1.2 g/l)

Total weight of dye pad solution: 50 gm

Chempad:

Sodium hydroxide: 28 cc of 1% solution

Sodium dithionite: 5.7 gm

Total weight of chempad solution: 50 gm

The dyeing sequence was:

Dye pad — dry at 100-110^{o}C for 5 minutes — chempad — steam for 15 minutes — cold rinse — soap — wash — air dry

The evaluation of K/S values of the dyed fabrics was performed as described in Section 6.8, and fastness properties were quantified as described in Sections 6.9 – 6.11.

6.15 Continuous Pad-Dry Heat Simulation Dyeing of Unmodified PP Fabrics

The continuous pad-dry heat process is currently in place for the disperse coloration of polyester and polyester blend fabrics using the Thermosol® method at a temperature of ~ 200^{o}C to sublime the low molecular weight dyes into the fiber [43]. The existing Thermosol® process was deemed a candidate for development of a continuous pad-dry heat method for the acid leuco vat dye coloration of generic PP fabrics, albeit at a lower temperature than that used for sublimation disperse dyeing of polyester (130^{o}C maximum for PP (MP of ~169^{o}C)). Thus the importance of dyeing PP constructions in the fabric dyeing industry motivated the development of a modified version of the Thermosol® method for PP coloration which requires a lower thermal fixation

temperature (130°C) without any substantial modification of equipment or process to the current Thermosol® method.

The optimized process was based on the concept described by A. V. Mishchenko et al. [35], who demonstrated that dry heat treatment (140°C) accelerates the diffusion of acid leuco vat dyes into the amorphous regions of the unmodified PP fiber. The optimized dyeing conditions were:

Fabric weight: 10 gms

Amount of dye: 2.85 gm (based on 70% pickup and 8% owf)

Sodium hydroxide: 14 cc of 1% solution

Sodium dithionite: 2.85 gm

Albaflow pad 01 (wetting agent of Huntsman Chemical Company): 3 cc of 1% solution (1.2 g/l)

Total weight of vat acid pad solution: 25 gm

The PP fabric was dipped into the vat acid solution and squeezed 2-3 times in order to perform the padding process. The dyeing sequence was:

Vat acid pad — oven dry heat treat at 130°C for 10 minutes — cold rinse — soap — wash — dry

The evaluation of K/S values of the dyed fabrics was performed as described in Section 6.8, and evaluation of fastness properties was performed as described in Sections 6.9 – 6.11.

CHAPTER 7: RESULTS AND DISCUSSION

7.1 Solubility Parameter Calculations

The chemical structures of oxidized vat dyes were obtained from the Colour Index, 1971 Edition [54]. The chemical structures of the corresponding reduced acid leuco vat dyes were determined using the general hydrosulfite/hydroxide reaction. The Fedors group contribution method was applied after structural analysis of the acid leuco vat dyes to compute the solubility parameter. The table of atomic and group contributions to energy of vaporization and molar volumes from Fedors was used in this computation [9].

Table 7.1 shows the calculated solubility parameters (SPs) for oxidized and reduced vat dyes in which Vat Red 15, Vat Orange 7, Vat Yellow 2, Vat Blue 18 and Vat Orange 1 have the lowest values. The solubility parameter of PP was calculated to be 8.1 $(cal/cm^3)^{1/2}$. Since Vat Red 15 and Vat Orange 7 are cis- and trans- isomers, respectively, the two molecules yielded equal solubility parameters.

Table 7.1. Calculated Solubility Parameters of Vat Dyes Using Fedors' Method [9]

C.I. Name of Dye	C. I. Constitution Number	Calculated SPs $(cal/cm^3)^{1/2}$ for Keto Form	Calculated SPs $(cal/cm^3)^{1/2}$ for Acid Leuco Form
Vat Red 1	73360	13.9	16.0
Vat Yellow 2	67300	13.7	15.0
Vat Blue 6	69825	15.3	18.6
Vat Orange 1	59105	13.0	14.6
Vat Blue 1 (Indigo)	73000	13.9	16.7
Vat Brown 1	70800	15.5	19.3
Vat Red 15	71100	14.2	14.4
Vat Yellow 33	65429	14.3	16.0
Vat Red 13	70320	13.4	14.8
Vat Orange 7	71105	14.2	14.4
Vat Yellow 4	59100	13.6	15.6
Vat Violet 1	60010	12.1	14.8
Vat Violet 13	68700	14.9	16.6
Vat Black 27	69005	15.1	17.5
Vat Green 8	71050	15.3	19.1
Vat Orange 2	59705	13.4	14.8
Vat Blue 18	59815	13.1	14.5
Vat Green 1	59825	13.5	14.9

Table 7.1 Continued

Vat Red 10	67000	15.1	18.4
Vat Orange 15	69025	14.6	16.7

7.2 Chemistry of Acid Leuco Dyeing

The four stages of reduction of C. I. Vat Orange 1 dye (Fig. 7.1) indicate that excess sodium hydrosulphite acts as an acid in addition to being a reducing agent for the carbonyl groups, and the chemical thus converts the alkaline leuco form of vat dye (II) into first the monoioninc leuco form (III) and, with further addition of sodium hydrosulphite, into the nonionic (acid leuco) form (IV):

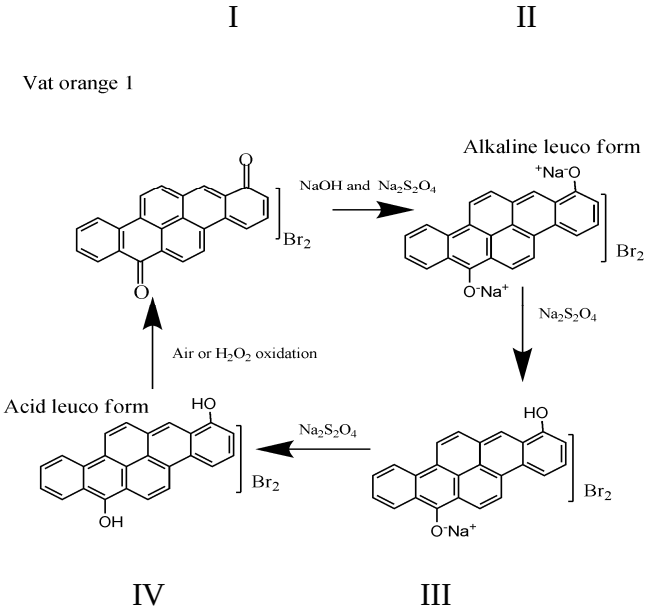


Figure 7.1. Various Stages of Conversion of Vat Orange 1 from the Keto to the Acid Leuco Structure: (I) Original Keto Structure; (II) Alkaline Leuco; (III) Monoionic; and (IV) Acid Leuco

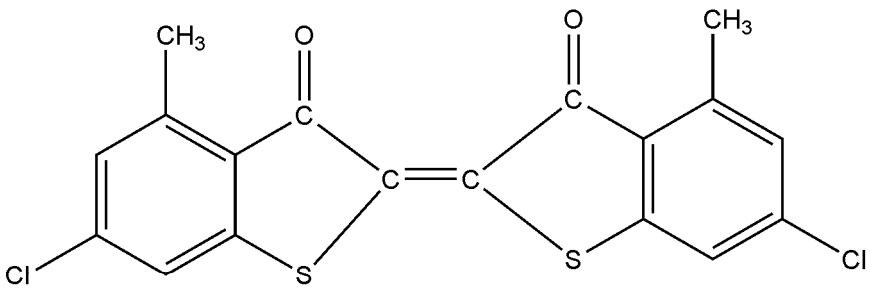
The neutral acid leuco form has been reported as having affinity with hydrophobic fibers such as polyester and PP [38,44,45].

7.3 Chemical Structures of Vat Dye Candidates for the PP Single-Stage, Acid Leuco Vat Dyeing Process

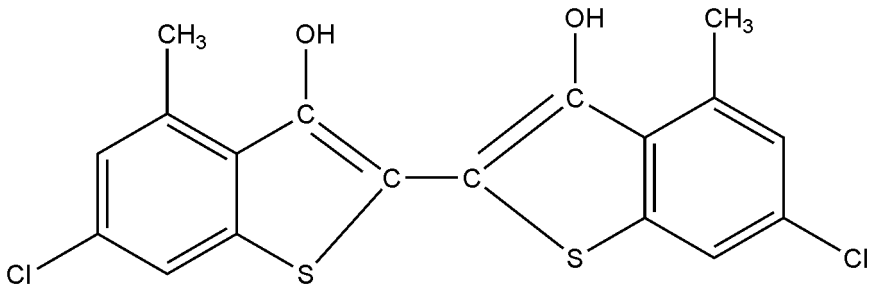
Figure 7.2 shows the conversion of a vat dye into its acid leuco form with the action of sodium hydroxide and excess sodium hydrosulphite. The acid leuco forms were utilized to calculate the solubility parameters of the vat dyes using Fedors' group contribution method (Table 7.1).

From the Colour Index search, the chemical structure of C. I. Vat Blue 8 deemed it a candidate for the dye trichromatic series (Figure 7.2 e). The SP for Vat Blue 8 was calculated in its acid leuco form to be 15.4 $(cal/cc)^{1/2}$, which was lower than those of Vat Blue 6 (18.6 $(cal/cc)^{1/2}$) and Vat Blue 1 (16.7 $(cal/cc)^{1/2}$). The predicted mixing energy was also much lower for Vat Blue 8 (10.2 kcal/mole) than Vat Blue 6 (22.1 kcal/mole), further strengthening the theory that Vat Blue 8 could be a more viable performer than Vat Blue 6 in the trichromatic series. However, an exhaustive search of dye vendor sources revealed that Vat Blue 8 is currently not commercially available on the world market, thus precluding its experimental confirmation as a viable vat blue colorant for generic PP.

Vat red 1



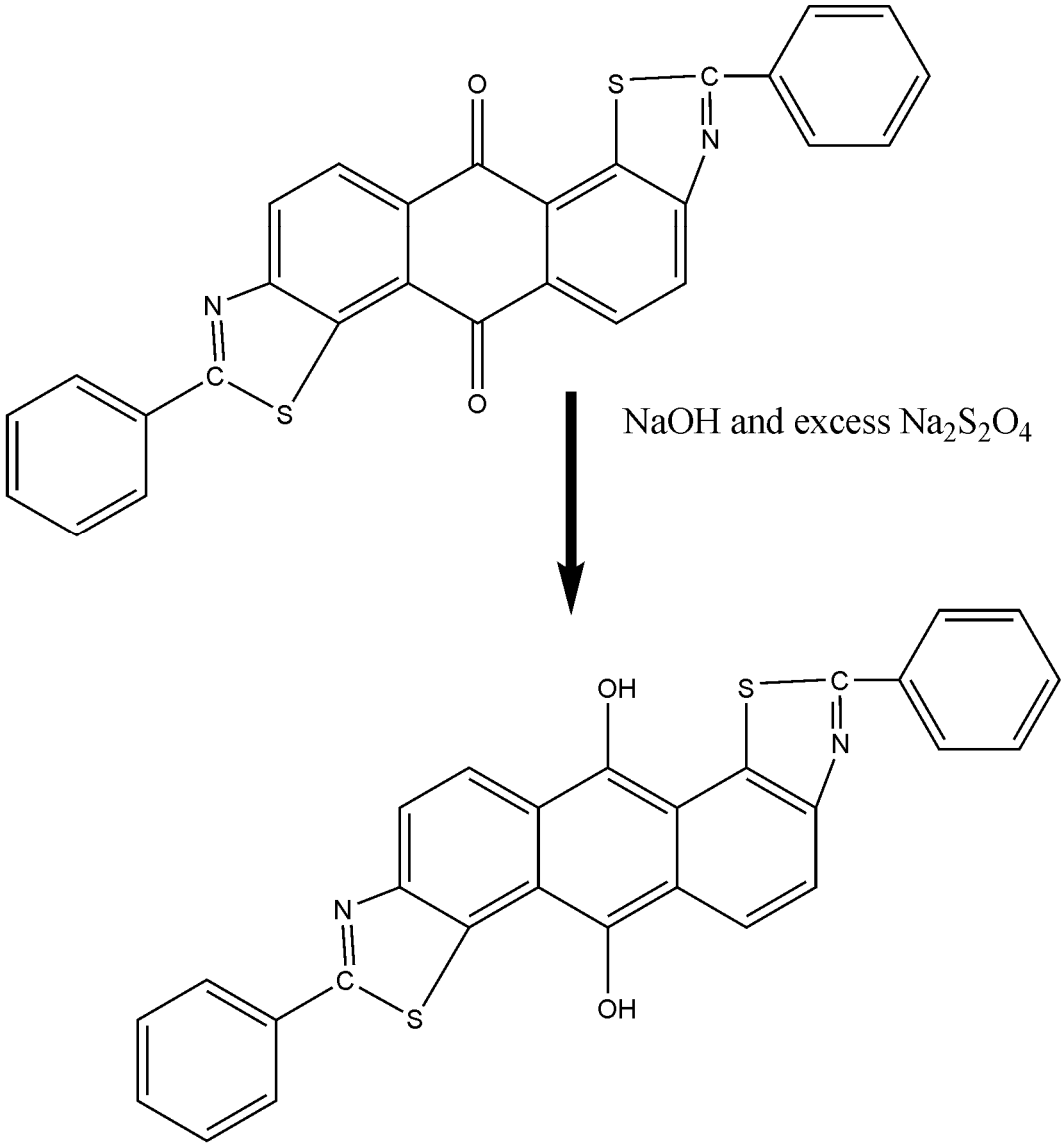
NaOH and excess $Na_2S_2O_4$



Acid leuco form of Vat red 1

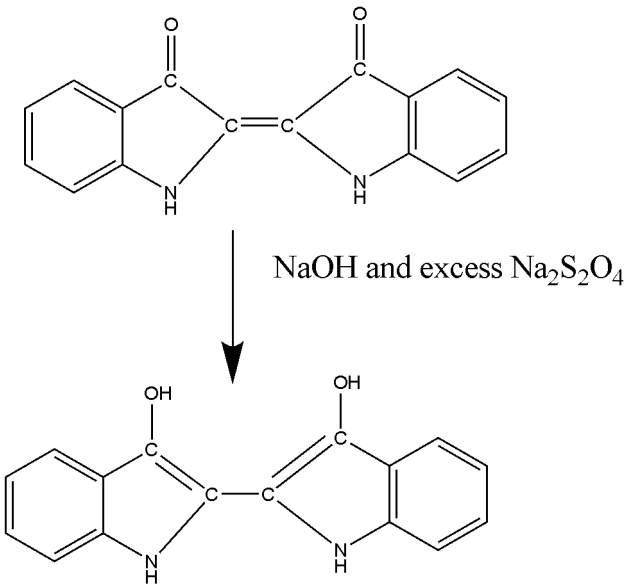
(a)

Vat yellow 2



(b)

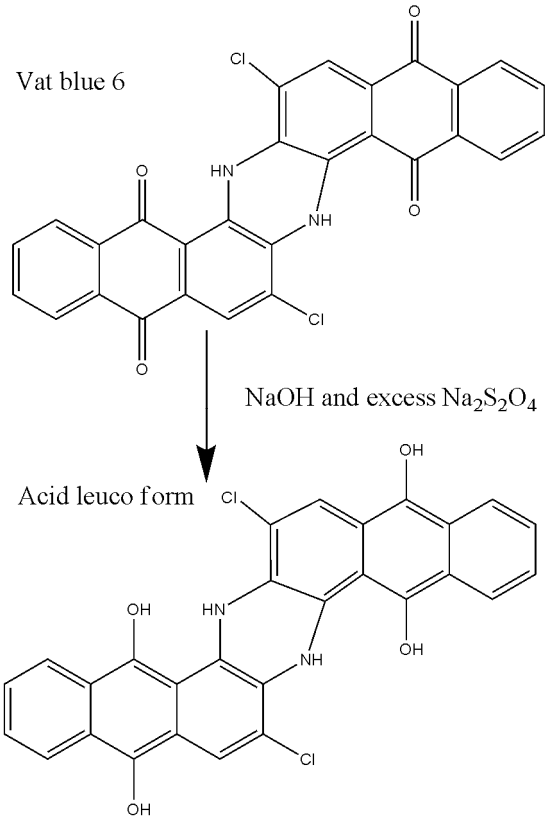
Vat blue 1



Acid leuco form of Vat blue 1

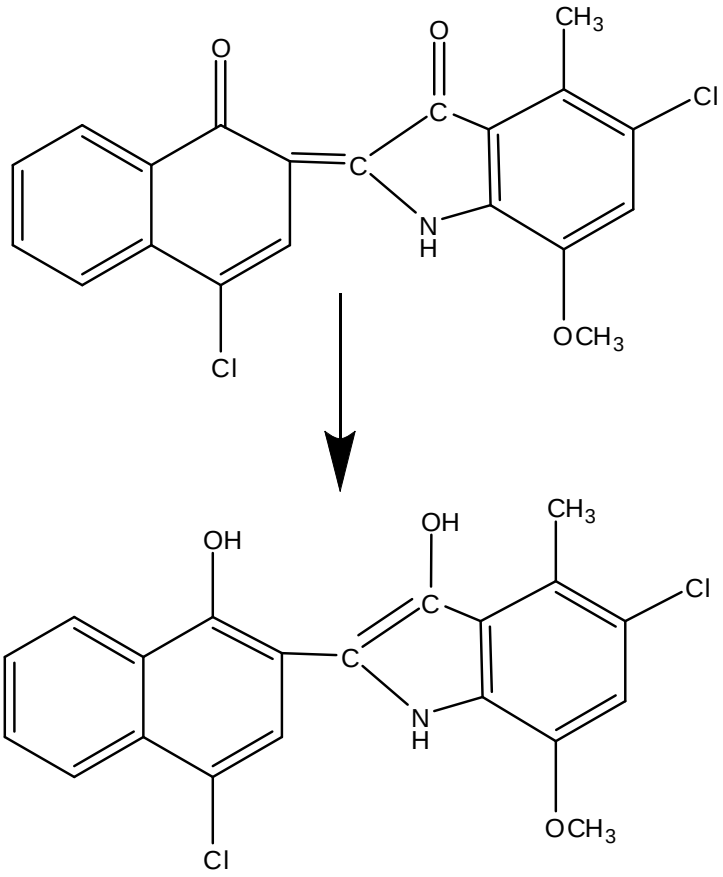
(c)

Vat blue 6



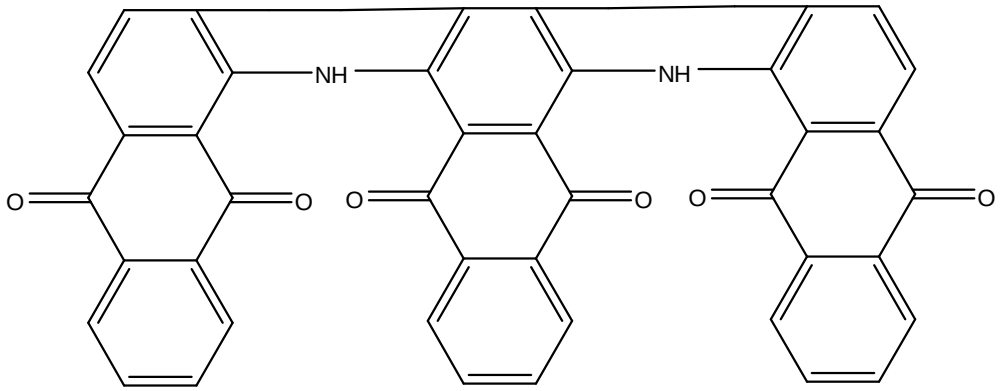
(d)

Vat blue 8, C.I. # 73800



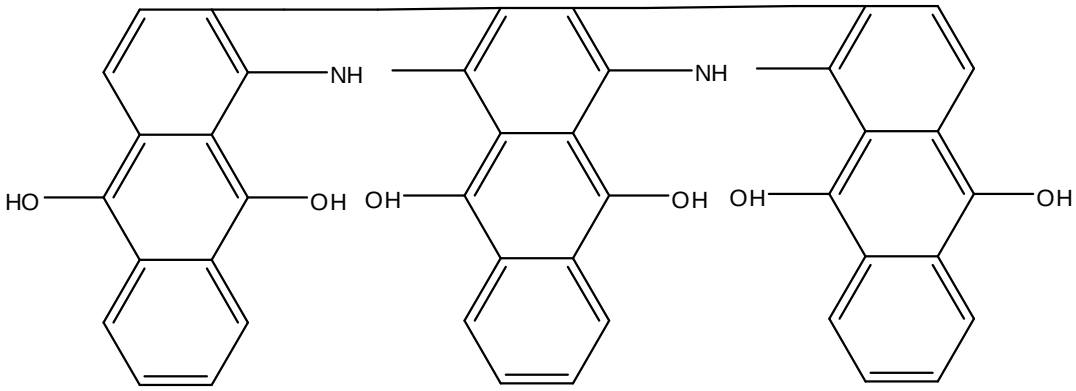
(e)

Vat brown 1



NaOH and excess $Na_2S_2O_4$

Acid leuco form of vat brown 1

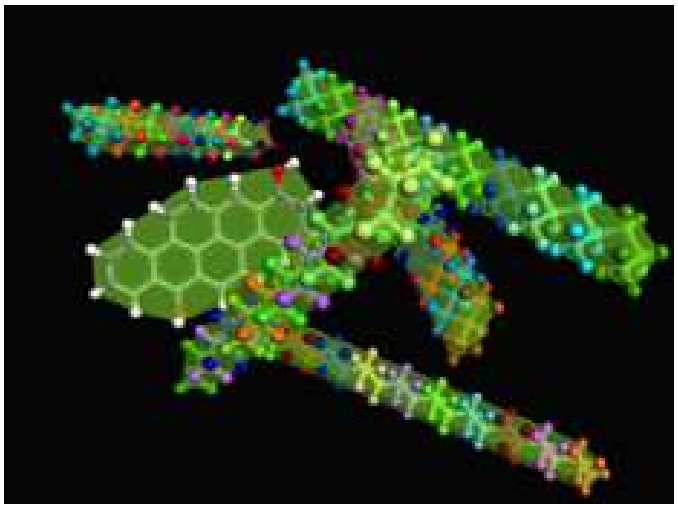


(f)

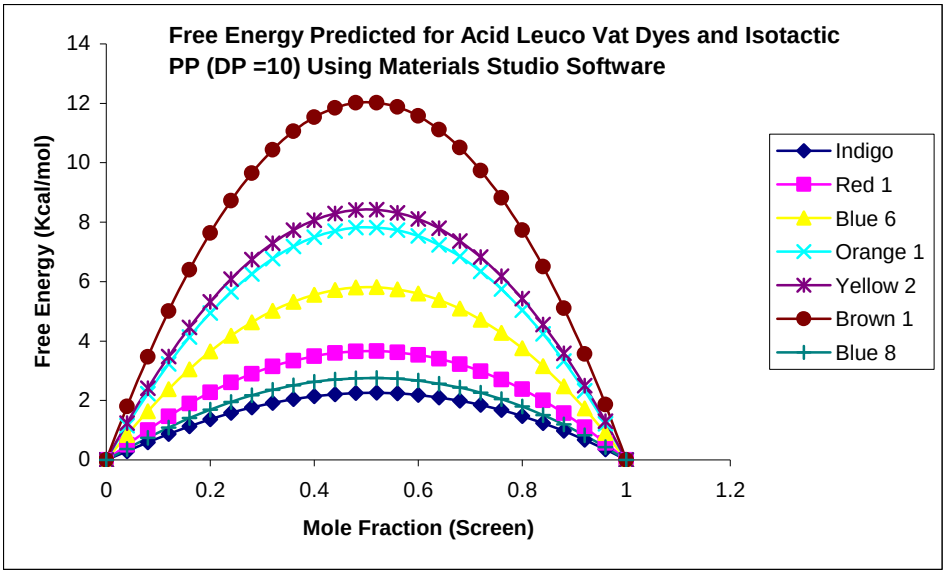
Figure 7.2. Conversion of Oxidized Vat Dye Keto Structures into Reduced Acid Leuco Structures: (a) Vat Red 1; (b) Vat Yellow 2; (c) Vat Blue 1 (Indigo); (d) Vat Blue 6; (e) Vat Blue 8; and (f) Vat Brown 1

7.4 Predicted Free Energy of Mixing of Acid Leuco Vat Dyes at 90°C Using Accelrys' Materials Studio® Software

Mixing energies of different acid leuco vat dyes with isotactic PP chain of DP=10 were predicted using Accelrys' Materials Studio® (MS) software. The Blends Analysis Feature of the MS software was used to perform dye-PP mixing simulations. The results in Figure 7.3 and Figure 7.4 demonstrated that the dyes C. I. Vat Blue 1, Vat Blue 8, Vat Red 1, and Vat Blue 6 had the lowest free energy / interaction parameters of mixing with PP. Vat Orange 1 and Vat Yellow 2 were intermediate in the parameters, while Vat Brown 1 had the highest free energy / interaction parameter of mixing. Vat Brown 1 was thus predicted to have poorer interactions with isotactic PP and resulting poorer exhaustion and color strength (K/S value) properties than the other dye candidates, predictions that were later confirmed by the exhaust batch dyeing experimental data.



(a)



(b)

Figure 7.3. (a) 3-D space Configuration of Vat Orange 1 Interacting with Isotactic PP in Materials Studio Workspace; (b) Free Energy vs. Mole Fraction of Different Dyes with PP at 363^{o}K Predicted Using Materials Studio® Software

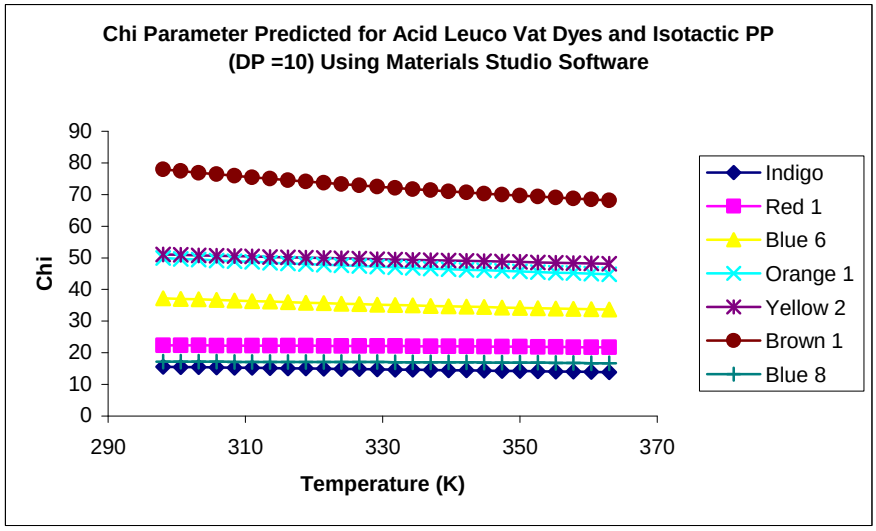


Figure 7.4. Interaction Parameter Chi vs. Temperature for Different Dyes with PP Predicted Using Materials Studio® Software

7.5 K/S Value Determinations

The Ultrascan XE sensor was standardized using a light trap and the standard white tile. The sensor was tested for accuracy before PP fabric measurements by scanning the diagnostic green tile, and then comparing the X, Y, Z tristimulus values obtained with the values printed on the green tile. Ten readings taken at different places were recorded for each of the dyed fabric samples, and the average of the ten readings was computed to derive the K/S value for each sample at the wavelength of minimum fabric reflectance. The K/S results in Table 7.2 revealed a correlation with the blend miscibility approach for the candidate six vat dyes, e.g., C. I. Vat Brown 1 gave the least color transfer onto the PP fabric due to its very high solubility parameter/mixing energy.

Table 7.2. Final K/S Values of PP Fabrics Colored by Single Stage Vat Acid Leuco Dyeing Method (8% owf)

C.I. Name of Dye	Wavelength of Minimum Reflectance (nm)	K/S at Wavelength of Minimum Reflectance	SP (Acid Leuco Form) $(cal/cm^3)^{1/2}$
Vat Red 1	510	4.4	16.0
Vat Blue 6	600	3.9	18.6
Vat Yellow 2	420	2.1	15.0
Vat Orange 1	440	5.0	14.6
Vat Blue 1	640	6.1	16.7
Vat Brown 1	400	1.7	19.3

The K/S versus % owf plot detailed that for all dyes, increasing the amount of colorant in the dyebath resulted in a gradual color buildup on the dyed fabric, followed by saturation (Figure 7.5). K/S values of the colored fabrics with the colorants of the trichromatic series plus orange exhibited similar K/S plots, whereas those dyed with Vat Blue 1 exhibited much higher K/S values, reinforcing the compatibility of the component colorants of the trichromatic series plus orange colorants in PP fabric dyeing, along with the incompatibility of Vat Blue 1 with the group.

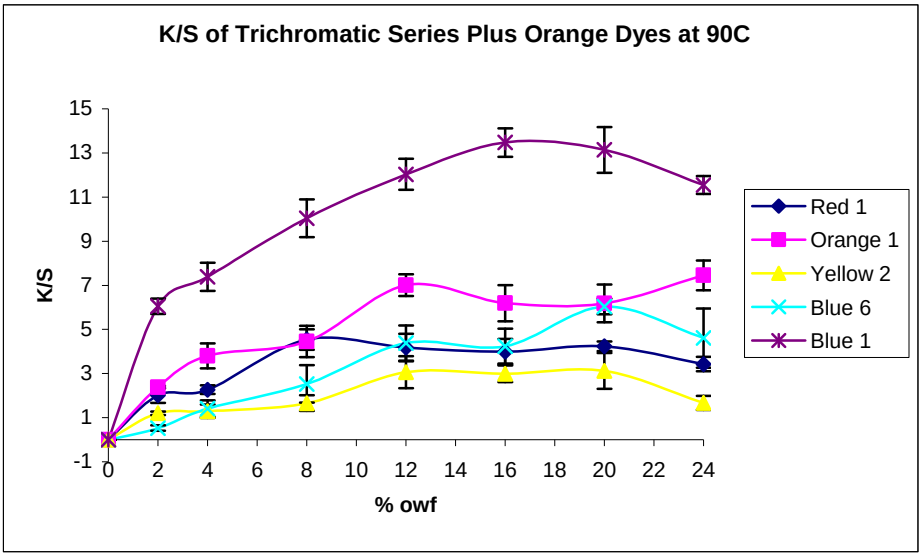


Figure 7.5. K/S Values at Wavelengths of Minimum Reflectance versus % owf for Acid Leuco Vat Dyed PP Fabrics

7.6 Correlation of Experimental K/S Values with Calculated Acid Leuco Dye Solubility Parameters and Predicted Mixing Energies

Figure 7.6 showed the correlation between K/S values of dyed PP fabrics and calculated SP/predicted mixing energies of six acid leuco vat dyes. Upon increasing solubility parameter and mixing energy from Vat Blue 1 to Vat Brown 1, the K/S value decreased. This correlation demonstrated the viability of the theoretical approaches (calculated SP and predicted mixing energy) to screening viable vat dye candidates for the coloration of generic PP.

The predicted mixing energy for Vat Orange 1 was high, but the corresponding high experimental fabric K/S value and low acid leuco vat dye SP value created an anomaly (Figure 7.6). The discrepancy was explained by the more complicated, high molecular weight chemical structure of C. I. Vat Orange 1 compared to the other certified dyes (MW = 468 g/mole, six fused aromatic rings in a benzenoid structure with a plane of symmetry running through the molecule, a dibromine salt, etc., Figure 7.1). Figure 7.3(a) models the difficulty in placing the Vat Orange 1 molecule within the polymeric chains of PP in the amorphous regions. In addition, utilizing the "like dissolves like" rule of organic chemistry and designating PP as the solvent and the Vat Orange 1 as the solute, the highly aromatic nature of the dye dictates poor compatibility with the aliphatic PP chains. Utilizing these two factors, the Materials Studio® Software predicted a comparatively high mixing energy between PP and Vat Orange 1 (Figure 7.3(b)). With the experimentally-observed high K/S value for the dyed fabric, however, the low SP of Vat Orange 1 (14.6 $(cal/cc)^{1/2}$) was a more accurate predictor of the good compatibility of the colorant with PP than was the mixing energy (Figure 7.6).

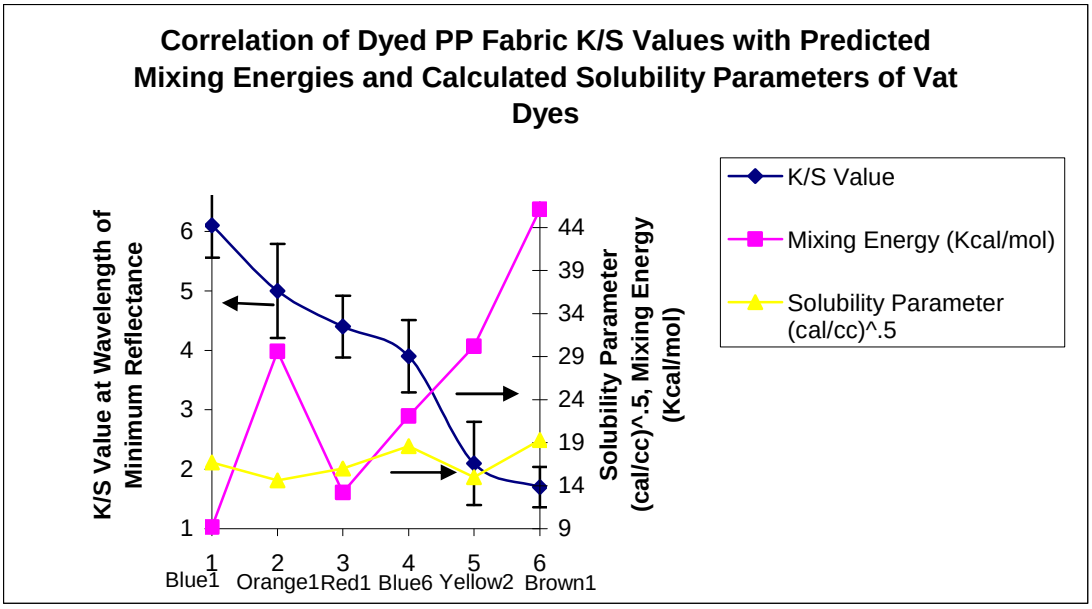


Figure 7.6. Correlation of Dyed PP Fabric K/S Values with Calculated Acid Leuco Dye Solubility Parameters and Predicted Mixing Energies

7.7 Evaluation of Fastness Properties

7.7.1 Fastness to Crocking

Crock fastness was determined using the electronic crock meter with 10 complete cycles in both dry as well as wet conditions according to AATCC Standard Test Method 8-2004. Vat Blue 6 exhibited less resistance to crocking as it stained the cotton cloth square to a rating of 3-4, whereas Vat Orange 1, Vat Red 1, Vat Blue 1 and Vat Yellow 2 all showed good to excellent crocking resistance (Table 7.3). The higher crock fastness ratings in the wet condition to that of the dry condition was attributed to the reduction in the frictional force between the low surface energy PP fabric and the rubbing finger of the crock meter caused by the lubricating effect of water at the interface.

Table 7.3. Crock Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Orange 1	4	4-5
Vat Yellow 2	4-5	4-5
Vat Blue 6	3-4	4
Vat Red 1	4	4-5
Vat Blue 1	4	4

7.7.2 Fastness to Washing

Wash fastness of the dyed materials was determined by AATCC Standard Test Method 61-2003, no. 2A. The fastness ratings (Table 7.4) revealed that Vat Orange 1 exhibited excellent wash fastness on the PP fabric, whereas the other vat dyes yielded good, acceptable wash fastness properties to the PP fabric.

Table 7.4. Wash Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	5	5	5	5	5
Vat Yellow 2	5	4-5	4-5	5	4-5	5	4-5
Vat Blue 6	5	4-5	4-5	4-5	4-5	4-5	4-5
Vat Red 1	5	4-5	4-5	4	4-5	4-5	4-5
Vat Blue 1	5	4-5	5	4	4-5	5	4-5

7.7.3 Fastness to Dry-Cleaning (Perchloroethylene)

Dry-cleaning fastness of the dyed materials was determined by AATCC Test Method 132-2004. The fastness ratings confirmed that all of the certified vat dyes imparted good, acceptable dry-cleaning fastness properties to dyed PP fabric (Table 7.5).

Table 7.5. Dry-Cleaning Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	4-5	4-5	4-5	4-5	4-5
Vat Yellow 2	5	4-5	4-5	4-5	4	4-5	4-5
Vat Blue 6	5	4-5	4	4	4	4	4-5
Vat Red 1	4-5	5	4	4-5	4-5	4-5	4-5
Vat Blue 1	4-5	4-5	4	4-5	4-5	4-5	4

7.8 Cross-Sectional Micrographs of the Dyed Specimens

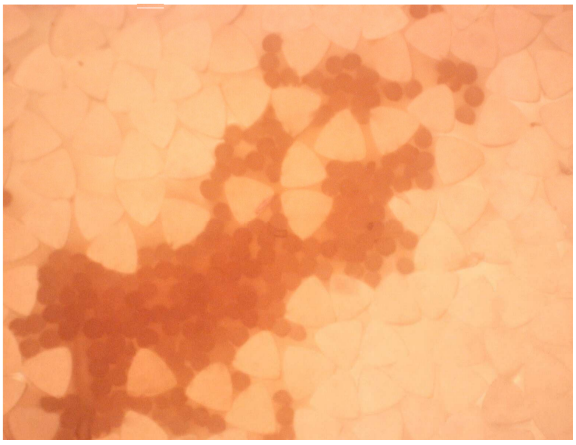
The PP fabric was dyed with acid leuco vat dyes and cross-sections were taken from yarns pulled from the fabric to assess through-yarn dye uniformity via microtoming. The cross-sectional pictures confirmed dye diffusion through the diameter of individual fibers colored on the outer surfaces of the yarns, i.e., “ring dyeing” was not evident, but not all of the fibers through the center of the yarn diameters were uniformly colored (Figure 7.7).

Poor dye bath circulation and pumping pressure through the yarns of the tightly-woven PP fabric on the Roaches lab dyeing machine were suspected as the causes of the through-yarn dye non-uniformity. To assess the theory, loose, generic PP fiber stock was obtained from FiberVisions, Inc. of Covington, GA, the fibers were batch dyed under the optimized acid leuco vat dyeing conditions, and cross-sectional pictures were made of the dyed fiber bundles. The cross-sectional pictures of the loose, dyed fibers revealed excellent through-diameter penetration of the dye in all of the individual fibers. The results confirmed that uneven dyeing of individual fibers mainly in the center of yarns in the tightly-woven PP fabric was due to inadequate dye liquor circulation through the multi-layer (4-5 layers) yarn/woven fabric structure in the Roaches Colortec Lab Dyeing Machine (Figure 7.8).

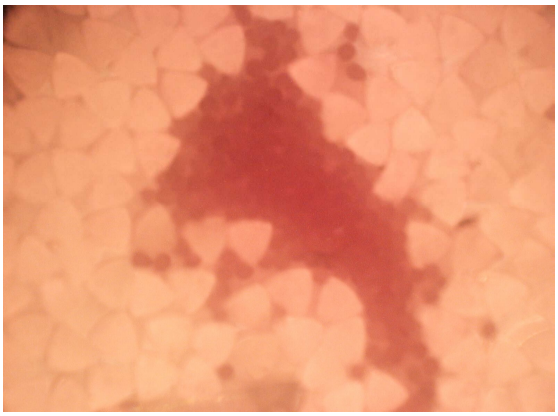
(a)

(b)

Figure 7.7. Cross-Sections of PP Yarns Extracted from Woven Fabrics Dyed with: (a) Vat Orange 1; and (b) Vat Red 1



(a)



(b)

Figure 7.8. Cross-Sections of Loose PP Fiber Bundles Dyed with: (a) Vat Orange 1; and (b) Vat Red 1

7.9 Dyeing Rate Plots

7.9.1 Dyeing Rate Plots for Single Dyeings

Acid leuco dyeings were performed for all of the single, certified vat dyes (8% owf) on the Roaches Colortec Dyeing Machine. Dye aliquots were taken from the dyebath at regular intervals, and for analysis, conversion of the acid leuco form into the

alkaline leuco form was achieved by adding additional sodium hydroxide and sodium dithionite. Percent exhaustion versus time plots were prepared for Vat Red 1, Vat Yellow 2, Vat Blue 6, Vat Blue 1 and Vat Orange 1 by measuring absorbances at their wavelengths of maximum absorbance: 540 nm, 515 nm, 665 nm, 400 nm and 475 nm, respectively. As shown in Figure 7.9, all of the dyes reached maximum exhaustion after ~40 minutes after the addition of the fabrics into the dyebaths at room temperature (28C).

At a rate of rise of 2.5C, the first 25 minutes of the plots incorporated the heat-up portion of the dyeing cycle, with the hold temperature of 90C reached at the end (Figure 7.9). The sorption-desorption fluctuation of the dyeings in the first ~5 minute of the cycles was attributed to the rapidly-rising temperature before steady-state conditions were achieved, e.g, see the Vat Yellow 2 plot in Figure 7.9.

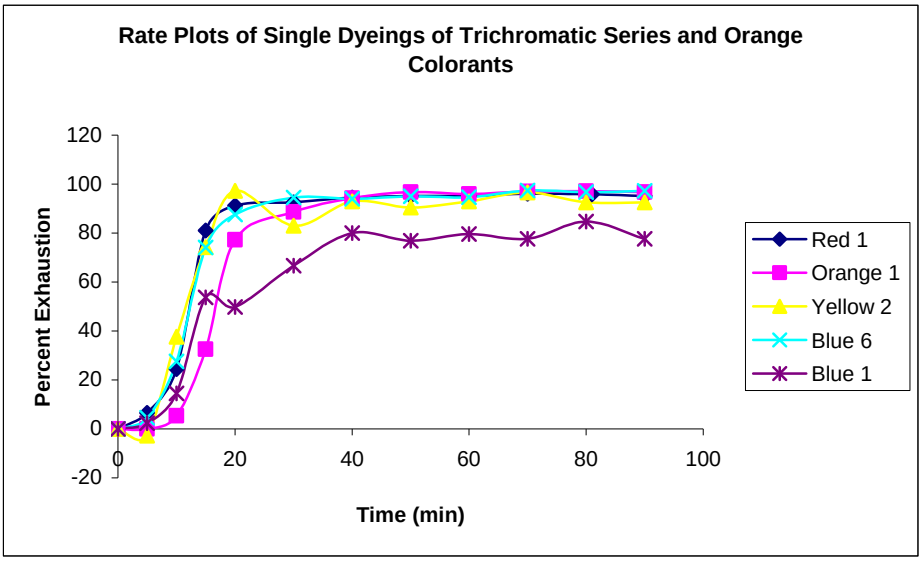


Figure 7.9. Dyeing Rate Plots for Trichromatic Series, Orange and Indigo Vat Colorants at 90^{o}C (Single Dye Colorations)

The dyeing affinity (μ) was determined by [55]:

$$-\Delta\mu = RT\ln\frac{D_f}{D_s} = RT\ln Kp \qquad \text{Eqn. 1}$$

R is universal gas constant and K_p is the partition coefficient.

The heat of dyeing was determined by [55]:

$$\Delta H = \frac{T_2\Delta\mu_1 - T_1\Delta\mu_2}{T_2 - T_1} \qquad \text{Eqn. 2}$$

The entropy of dyeing was calculated by [55]:

$$\Delta S = \frac{(\Delta H - \Delta\mu)}{T} \qquad \text{Eqn. 3}$$

The dyeing affinity was utilized as an absolute value in Eqn. 3. Diffusion coefficient (D) was calculated using [56]:

$$\frac{Dt_{1/2}}{r^2} \approx 0.063(1 - E_\infty)^n \qquad \text{Eqn. 4}$$

Here $t_{1/2}$ is the time of half-dyeing and r is the radius of the fiber (10 micrometers). The exponential n is related to equilibrium bath exhaustion (E_∞), which in turn is related to the partition coefficient (Kp) [56]:

$$E_\infty = \frac{Kp}{Kp + L} \qquad \text{Eqn. 5}$$

The liquor ratio of the dye bath is L, while n is related to E_∞ by [56]:

$$n \approx A\exp\left\{-h(1 - E_\infty)^m\right\} \qquad \text{Eqn. 6}$$

As per Etters, utilized values of the constants were [56]: A=1.91, h=0.34 and m=0.4.

The thermodynamic parameters for the single-colorant dyeings (trichromatic series plus orange) are tabulated in Table 7.6:

Table 7.6. Experimentally Determined Thermodynamic Parameters of Dyeing

Name of Dye	Partition Coef-ficent at 90°C	Dyeing Affinity at 90°C (Kcal/ mole)	Heat of Dyeing (Kcal/mole)	Entropy of Dyeing (Kcal/mole/ °C) at 90°C	Half Dyeing Time (min)	Diffusion Coefficient at 90°C (cm^2/s)
Vat Red 1	93	-3.3	-2.5	-0.06	12	$0.7x10^{-10}$
Vat Blue 6	61.4	-3.0	-1.0	-0.04	12	$0.7x10^{-10}$
Vat Yellow 2	88.3	-3.2	-1.8	-0.06	11	$0.7x10^{-10}$
Vat Orange 1	81.9	-3.2	-0.4	-0.04	16	$0.5x10^{-10}$

Dyebaths utilizing Vat Blue 1 showed the difficulty in measuring absorbance due to the facile air oxidation of the dye remaining in the residual liquor after opening the machine container. The oxidized dye particles did not reduce and dissolve completely, even after

adding excess sodium hydroxide and hydrosulfite to the cooled liquor. Calculation of percent exhaustion could thus not be performed for Vat Blue 1, and correspondingly the thermodynamic parameters could not be calculated.

The negative values of dyeing affinities and heats of dyeing confirmed the strong interactions between the acid leuco vat dyes and the PP fiber. Times of half-dyeing and diffusion coefficient values reinforced the compatibility of the dyeing rates of the certified vat dyes, an important factor in later combination (competitive) dyeings for shade generation. The heats of dyeing and dyeing affinities in Table 7.6 are of the same order of magnitude as the values reported by Bird et al.[31] for the disperse dyeing of unmodified PP, and by Mishchenko et al.[34] for the acid leuco vat dyeing of the fiber. The partition coefficient (Kp) values in Table 7.6 are significantly larger than those reported by Bird et al.[31] for the disperse dyeing of unmodified PP. However, the diffusion coefficients in Table 7.6 are almost one order of magnitude smaller than the reported values by Bird and Patel [31]. The significantly higher saturation values and lower diffusion coefficients for acid leuco vat dyeing of unmodified PP when compared to disperse dyeing of the fiber confirm that the larger molecular size of the acid leuco vat dyes compared to that of disperse dyes tend to cause the former to diffuse slower inside the amorphous polymeric regions. Significantly, the same larger molecular size aids in more effective physical "trapping" of the acid leuco vat dyes by the polymeric chains in the amorphous regions of the PP fiber, leading to superior (and acceptable) fabric fastness properties compared to those colored by smaller disperse dyes (see Tables 7.3-7.5).

The dye "easy-in, easy-out" transport phenomenon observed with disperse dyeing of PP is due to the comparatively smaller molecular size of the molecules compared to

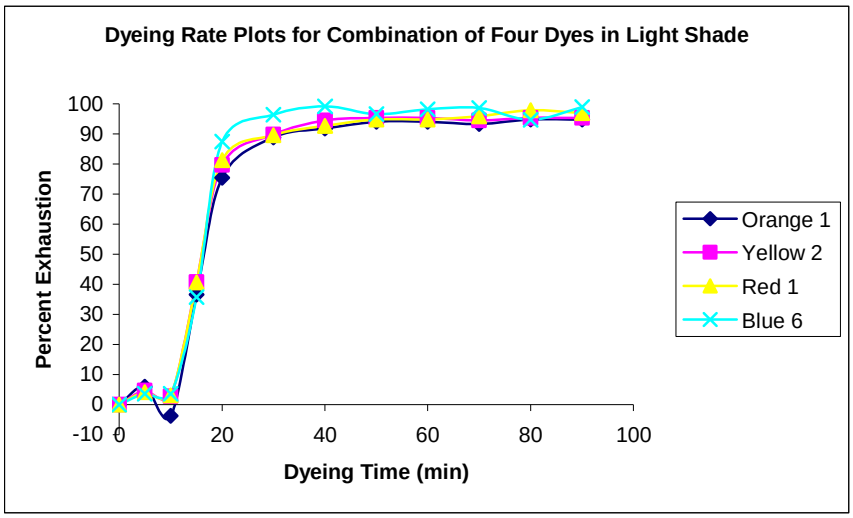
vat dyes. The molecular size discrepancy causes an increase in the saturation values and partition coefficients of acid leuco vat dyes on PP compared to disperse dyes. The fundamental dyeing mechanism for acid leuco vat colorants on generic PP is the same, however, to that of disperse dyeing of the fiber, i.e., a solid solution/pore filling mechanism of dye diffusion into the amorphous domains of the fiber, exhibiting a classical Nernst adsorption isotherm when Cf vs. Cs is plotted (see Fig.7.12).

7.9.2 Dyeing Rate Plots for Combination Dyeings

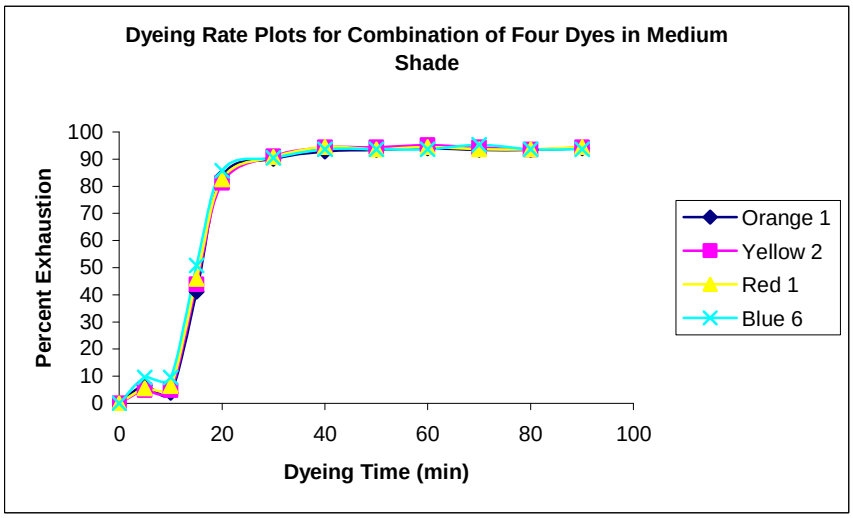
In order to investigate the compatibility of the trichromatic series plus orange dyes, the colorants were used in equal amounts to generate light, medium and dark shades on the generic PP woven fabric. Absorbance of each dye was recorded at selected times of dyeing (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90 minutes) at all four wavelengths of maximum absorbance: 540 nm, 515 nm, 665 nm and 475 nm for C. I. Vats Red 1, Yellow 2, Blue 6 and Orange 1, respectively, all converted to their alkaline leuco forms for analysis. The exhaustion of each dye was calculated by using the equation:

$$\%\,\text{Exhaustion} = \frac{(A_o - A_t)}{A_o} \times 100 \qquad \text{Eqn. 7}$$

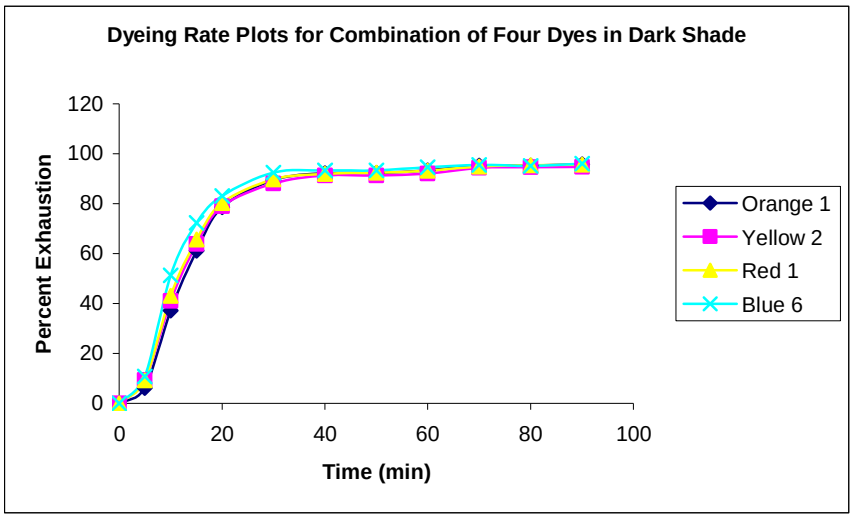
A_o was the absorbance before adding fabric into the dyebath, and A_t was the absorbance at dyeing time t. The dyeing rate plots confirmed the good compatibility of the trichromatic series plus orange colorants in light, medium and dark shades, as reflected by their similar rates of dyeing in combined (and thus competitive) situations (Figures 7.10-7.11).


Dyeing Rate Plots for Combination of Four Dyes in Light Shade
Percent Exhaustion
100
90
80
70
60
50
40
30
20
10
0
-10
0
20
40
60
80
100
Dyeing Time (min)
Orange 1
Yellow 2
Red 1
Blue 6

(a)

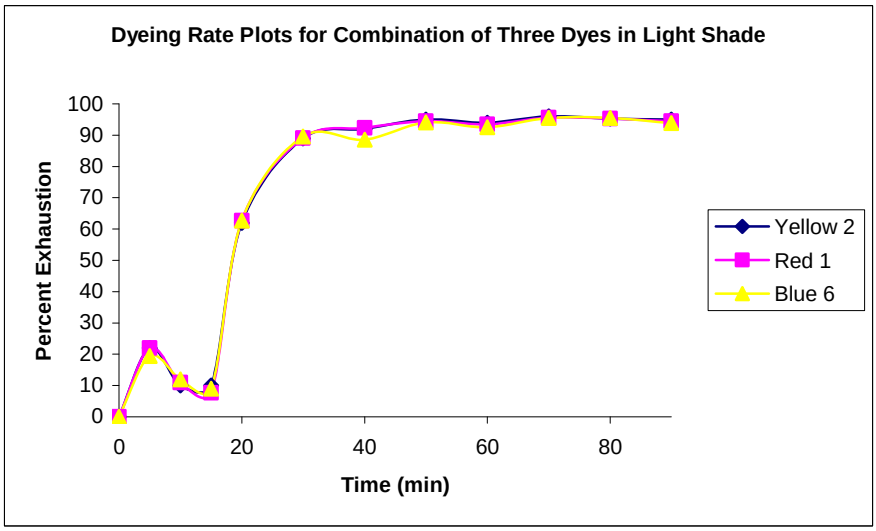

Dyeing Rate Plots for Combination of Four Dyes in Medium Shade
Percent Exhaustion
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Dyeing Time (min)
Orange 1
Yellow 2
Red 1
Blue 6

(b)

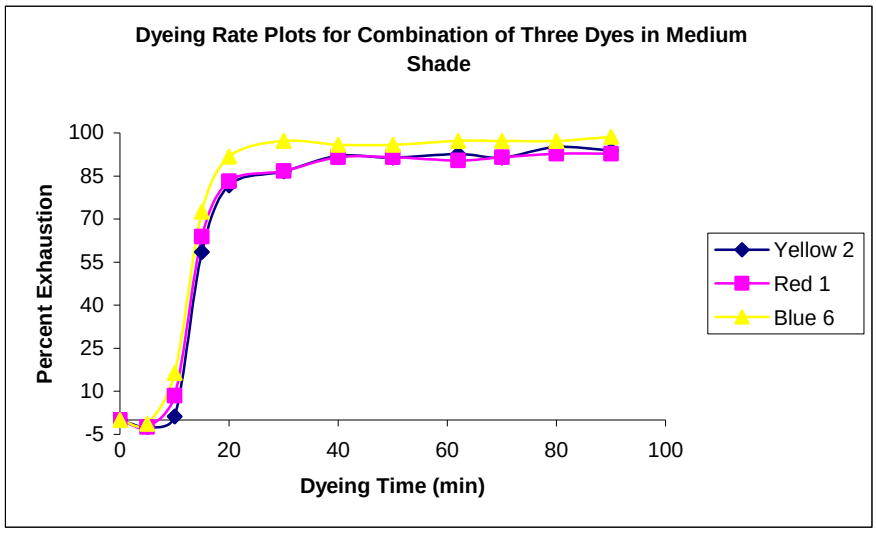


(c)

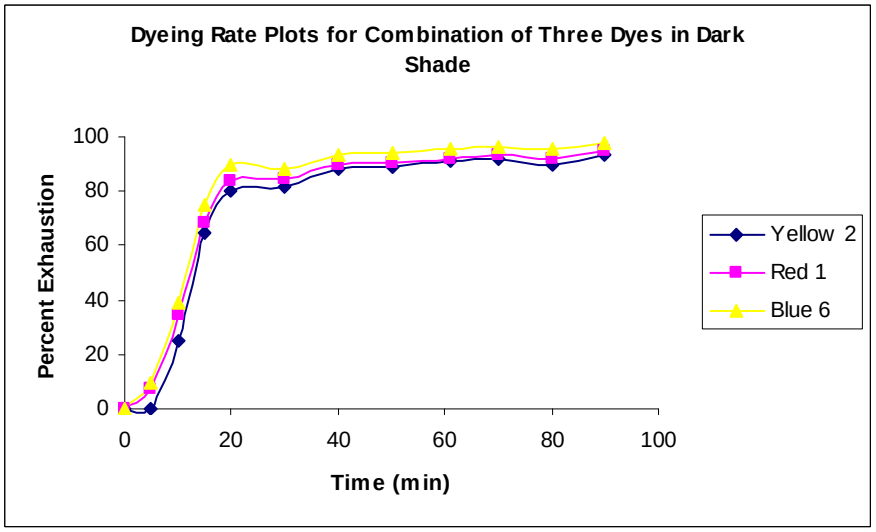
Figure 7.10. Dyeing Rate Plots for the Trichromatic Series plus Orange in: (a) Light Shade; 0.9% owf; (b) Medium Shade: 2.8 % owf; and (c) Dark Shade: 9.4 % owf



(a)



(b)



(c)

Figure 7.11. Dyeing Rate Plots for the Trichromatic Series in: (a) Light Shade: 0.7% owf; (b) Medium Shade: 2.8 % owf; and (c) Dark Shade: 10.6 % owf

As in the single colorant dyeings, the sorption-desorption instabilities exhibited in the first ~15 minutes were attributed to the rapidly-changing temperature of the bath created

by the 2.5C/minute rate-of-rise employed to reach the 90C hold temperature (25 minutes required, Figures 7.10-7.11).

7.10 Adsorption Isotherms

Figures 7.12 – 7.15 quantify the solid solution dyeing mechanism of the certified acid leuco vat dyes on unmodified PP, i.e., a classic Nernst adsorption isotherm is followed:

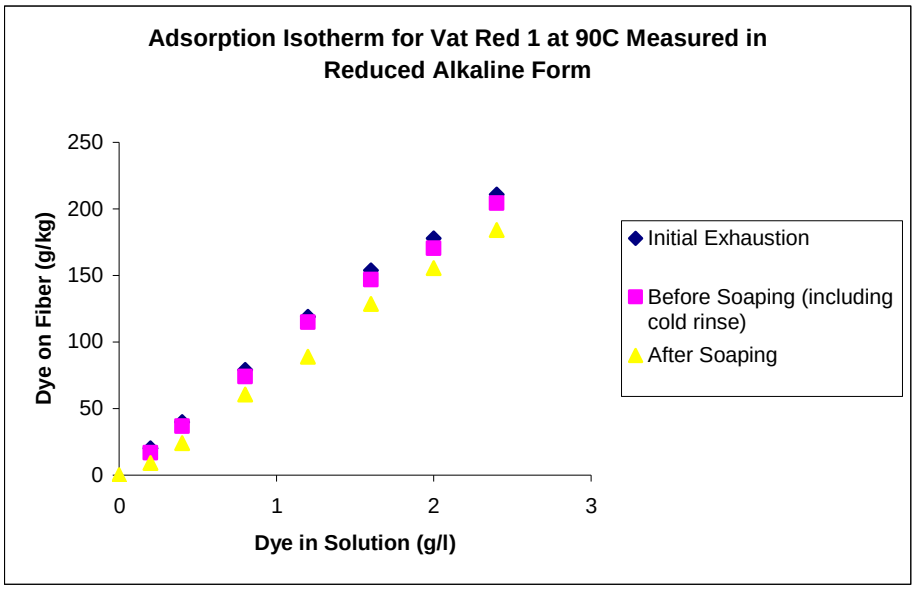


Figure 7.12. Adsorption Isotherm for PP Acid Leuco Dyeing with Vat Red 1 Using Single-Stage Dyeing Method

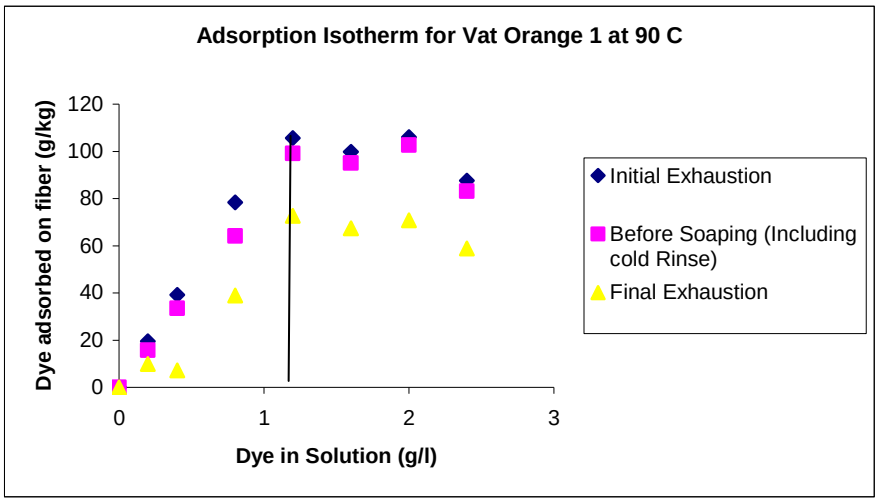


Figure 7.13. Adsorption Isotherm for PP Acid Leuco Dyeing With Vat Orange 1 Using Single-Stage Dyeing Method

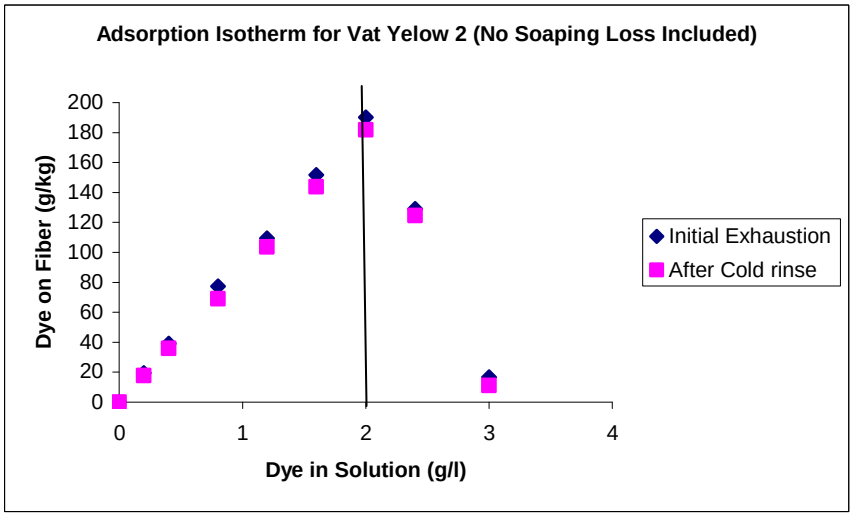


Figure 7.14. Adsorption Isotherm for PP Acid Leuco Dyeing with Vat Yellow 2 Using Single-Stage Dyeing Method at 90^{o}C

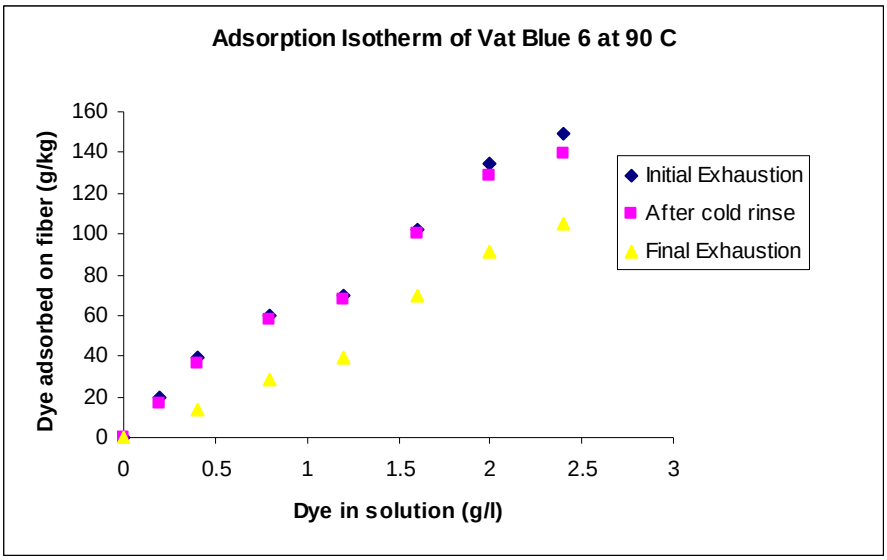
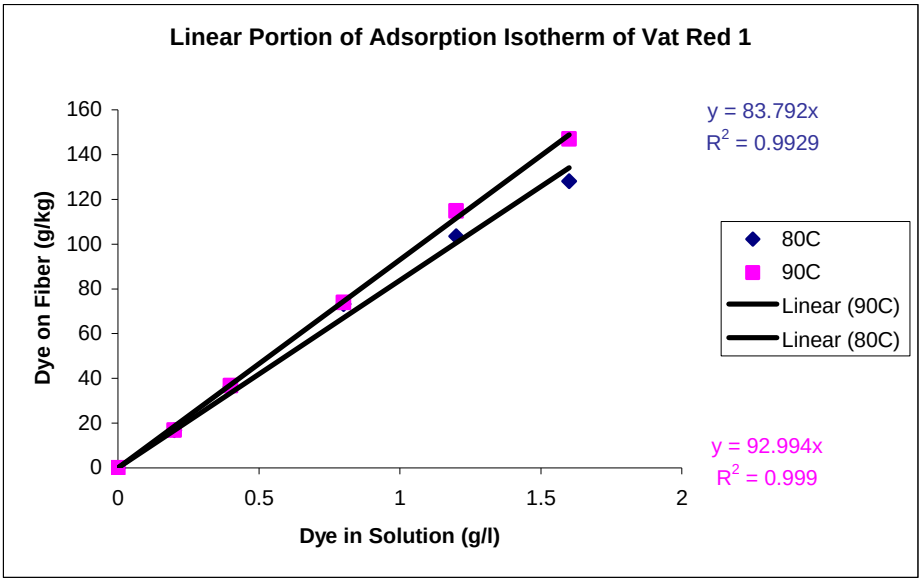


Figure 7.15. Adsorption Isotherm for PP Acid Leuco Dyeing With Vat Blue 6 Using Single-Stage Dyeing Method at 90^{O}C

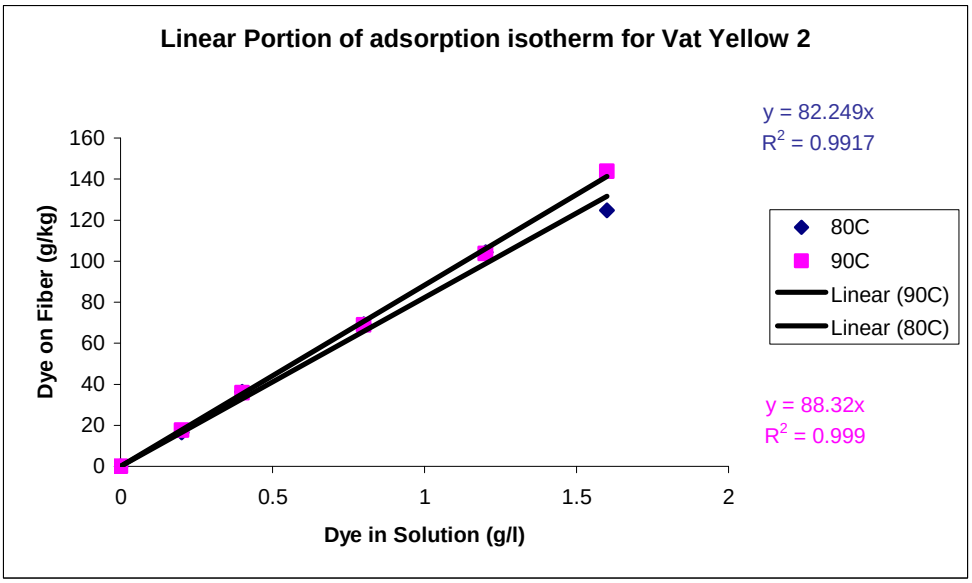
When the available "holes" within the PP fiber large enough to accommodate the vat dye molecules under the optimized dyeing conditions were filled, no further colorant could enter the structure, and thus the Cf vs. Cs plots abruptly plateaued, and further increases in Cs beyond the saturation point gave no further rise in Cf. This same dyeing mechanism was also followed in the disperse dyeing of polyester and cellulose acetate [57] and the cationic dyeing of Nomex fibers with the solvent-based STX System [58]. Dye uniformly transferred from the aqueous phase to the fiber phase in a linear fashion, and then reached saturation at the concentration of 1.2 g/l (12% owf) for Vat Orange 1 (Figure 7.13). For Vat Red 1 (Figure 7.12) and Vat Blue 6 (Figure 7.15), the dye adsorbed on the fiber continued to increase with the amount of dye in the bath up to the highest Cs tested (2.4 g/l).

The Figure 7.14 plot for Vat Yellow 2 formed an anomalous triangular shape: the dye adsorbed on the fiber increased linearly until 20 % owf (2.0 g/l), then suddenly dropped. Apparently, reduced molecules of the Vat Yellow 2 dye were being adsorbed on un-reduced particles of the still-oxidized dye at the high colorant concentrations instead of transferring onto the PP fiber. The amount of reducing agent was kept constant for all dye concentrations in the baths, and at the highest dye concentrations, the available reducing agent in solution was insufficient to reduce all of the colorant molecules (the molar reaction between hydrosulfite and dye is 2:1, with the latter possessing two ketone groups per molecule to reduce to hydroxyl groups). When the available hydrosulfite was fully reacted at the higher dye add concentrations, any unreduced dye molecules remained in the insoluble oxidized form as solid suspended particles, apparently able to adsorb the reduced dye molecules before they reached the fabric surface. To a much lesser extent, the Vat Orange 1 plot showed similar behavior at the highest Cs tested (Figure 7.13).

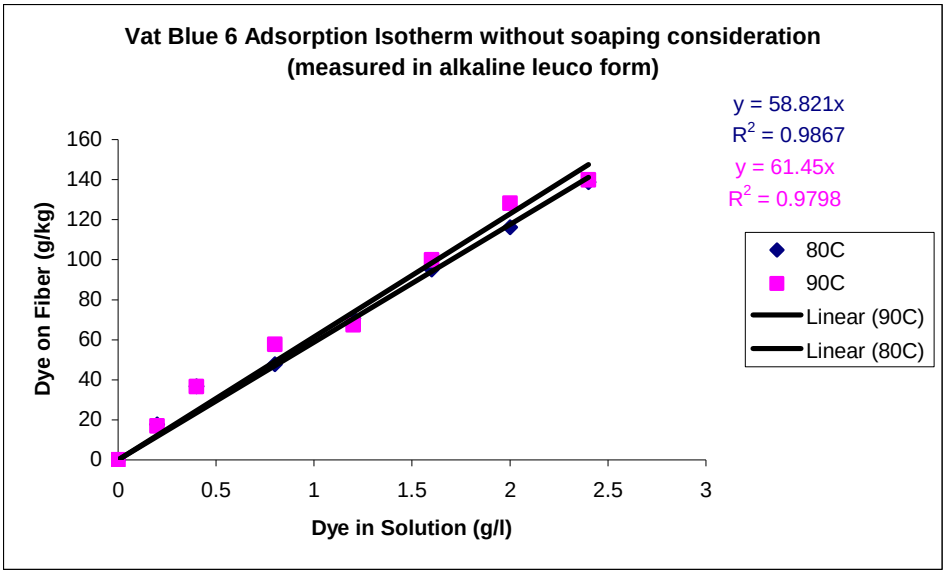
Figure 7.16 shows the linear portions of the adsorption isotherms of the certified acid leuco vat dyes at 90 and 80°C along with the corresponding linear fit equations. The slope of the straight line gave the value of the partition coefficient, which was used to calculate thermodynamic parameters such as heat of dyeing, dyeing affinity and diffusion coefficient. The slope of the plot was higher at 90°C that at 80°C for all the vat dyes (although the change was minimal for Vat Orange 1), confirming that dyeing is more favorable at 90°C due to higher mobility (i.e., higher kinetic energy) of the dye molecules in solution, thus resulting in higher mass transport of the colorants into the fibers.


Linear Portion of Adsorption Isotherm of Vat Red 1
y = 83.792x
R2 = 0.9929
y = 92.994x
R2 = 0.999
80C
90C
Linear (90C)
Linear (80C)
Dye on Fiber (g/kg)
Dye in Solution (g/l)
0
20
40
60
80
100
120
140
160
0
0.5
1
1.5
2

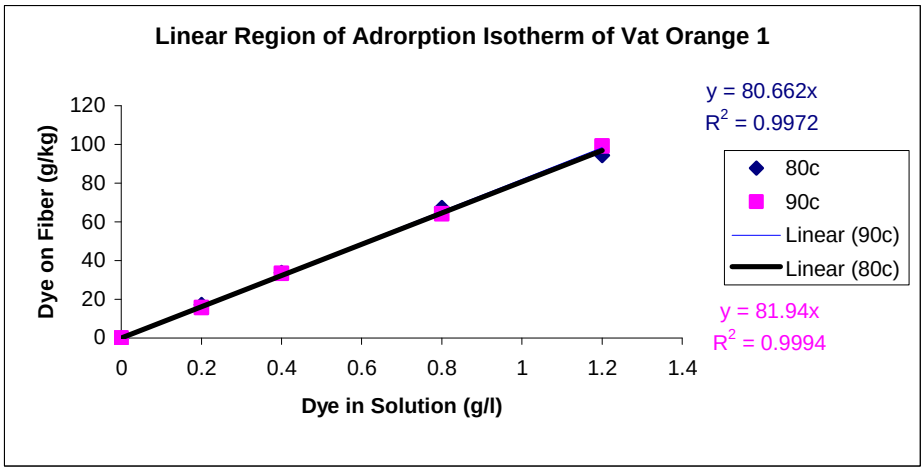
(a)


Linear Portion of adsorption isotherm for Vat Yellow 2
y = 82.249x
R2 = 0.9917
y = 88.32x
R2 = 0.999
80C
90C
Linear (90C)
Linear (80C)
Dye on Fiber (g/kg)
Dye in Solution (g/l)
0
20
40
60
80
100
120
140
160
0
0.5
1
1.5
2

(b)



(c)



(d)

Figure 7.16. Linear Portions of the Adsorption Isotherms of Trichromatic and Orange Vat Colorants at 90 and 80 C: (a) Vat Red 1; (b) Vat Yellow 2; (c) Vat Blue 6; and (d) Vat Orange 1

Figure 7.17 exhibits the overlapping linear portions of the adsorption isotherms for the trichromatic series plus orange vat colorants. The plot reinforces the compatibility of color buildup for the component dyes in combination.

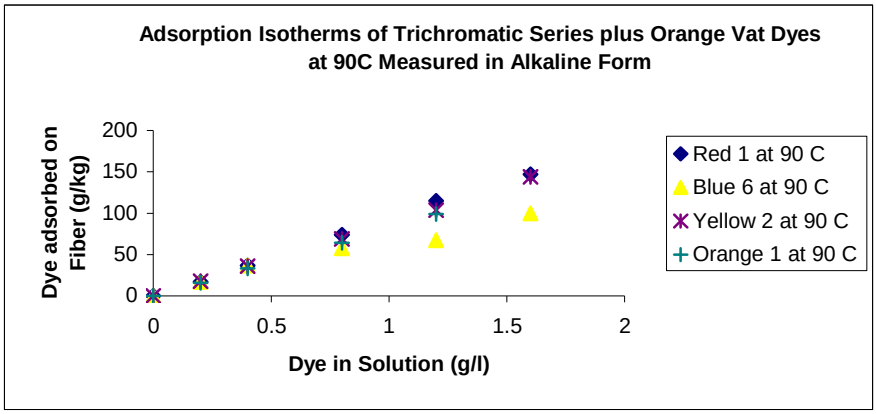


Figure 7.17. Overlapping Linear Portions of Adsorption Isotherms for PP Acid Leuco Dyeing with the Trichromatic Series plus Orange Vat Colorants at 90°C

7.11 Tensile Testing Results for Dyed and Undyed PP Textiles

Tensile tests of yarns extracted from the dyed and undyed (standard) woven PP fabrics were conducted on an Instron Model No. 5567 frame constant strain rate machine using Bluehill software. A strain rate of 60 mm/min and gauge length of 100 mm was used for all the yarn specimens. Five readings each for warp and weft were taken for all samples and the average of ten readings was calculated for each sample. The dyed samples did not suffer any significant change in load at break, tenacity at break and modulus at break as a result of the optimized, single-stage acid leuco vat dyeing procedure (Figures 7.18–7.20).

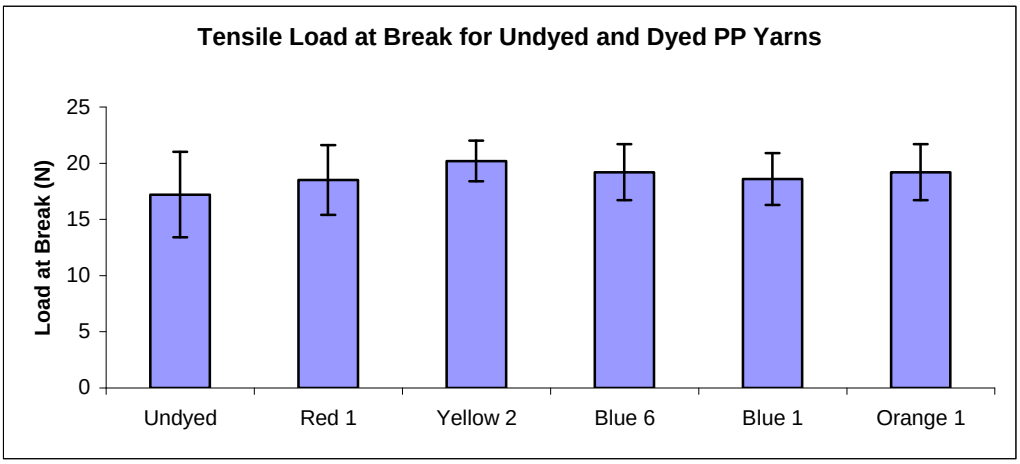


Figure 7.18. Tensile Load at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted From Woven Fabrics

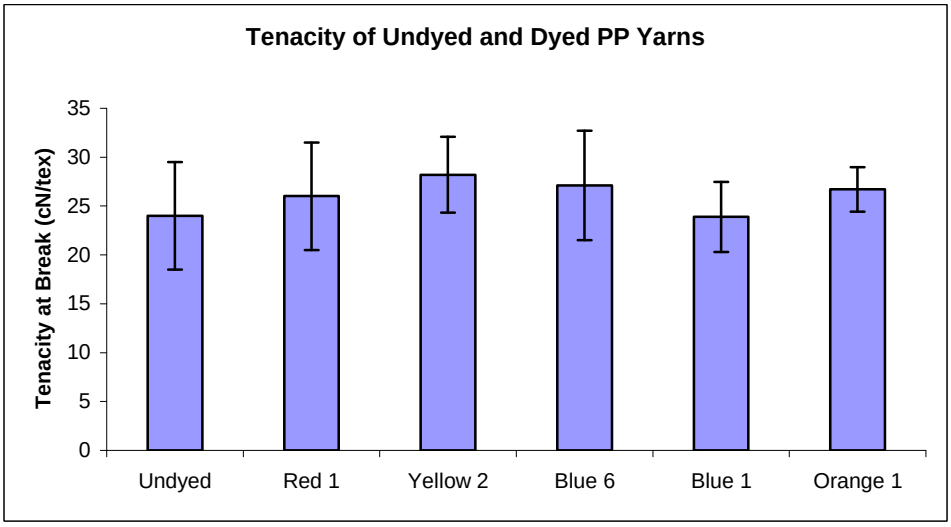


Figure 7.19. Tenacity at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted from Woven Fabrics

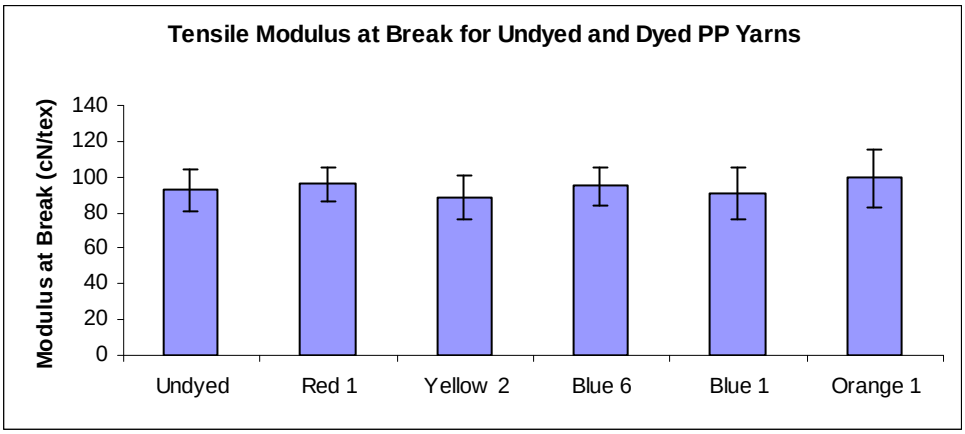


Figure 7.20. Tensile Modulus at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted from Woven Fabrics

7.12 X-Ray Diffraction Studies

In order to investigate the effect of the optimized, exhaust batch dyeing process on the solid-state-structure of the PP fiber, Wide-Angle X-ray Diffraction (WAXD) studies were conducted on a Rigaku Micromax-002 WAXS/SAXS system operating at a voltage of 45 kV and a current of 0.66 mA equipped with a Rigaku R-axis IV++ 2-D detection system. The analyses of the diffraction patterns were performed using AreaMax V. 1.00 and MDI Jade 6.1 software. The diffraction patterns (Figures 7.21-7.26), intensity vs. 2θ (Figure 7.27) and percent crystallinity data (Table 7.7) confirmed the physical testing data that no significant change in the degree of crystallinity of the PP fiber occurred as a result of the developed exhaust batch dyeing process.

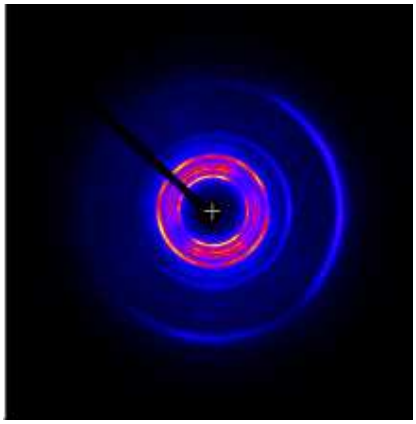


Figure 7.21. Wide Angle X-Ray Diffraction Pattern of Undyed PP Fabric

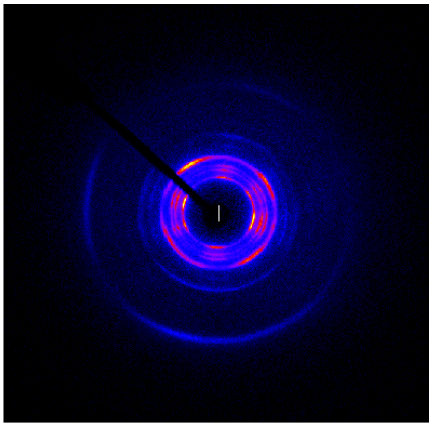


Figure 7.22. Wide Angle X-Ray Diffraction Pattern of PP Fabric Dyed with Vat Red 1

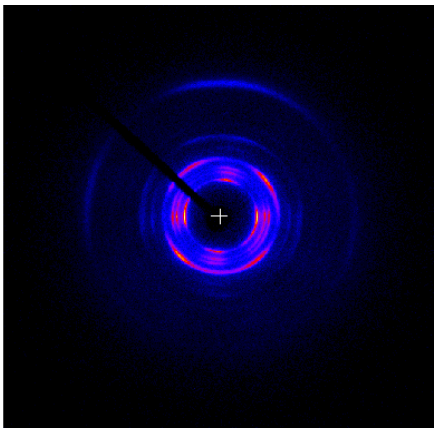


Figure 7.23. Wide Angle X-Ray Diffraction Pattern of PP Fabric Dyed with Vat Yellow 2

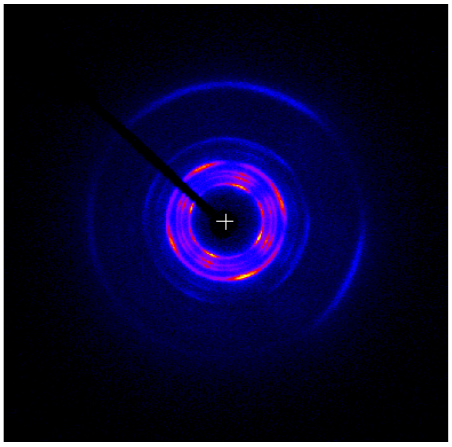


Figure 7.24. Wide Angle X-Ray Diffraction Pattern of PP Fabric Dyed with Vat Blue 6

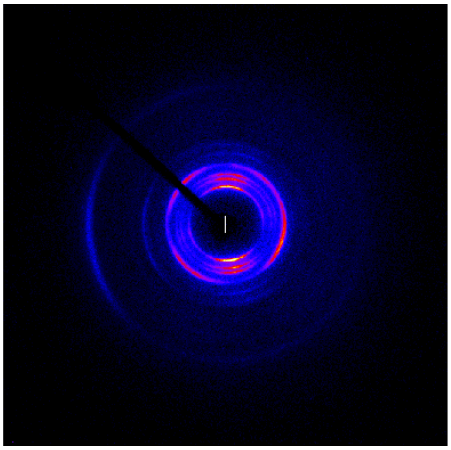


Figure 7.25. Wide Angle X-Ray Diffraction Pattern of PP Fabric Dyed with Vat Orange 1

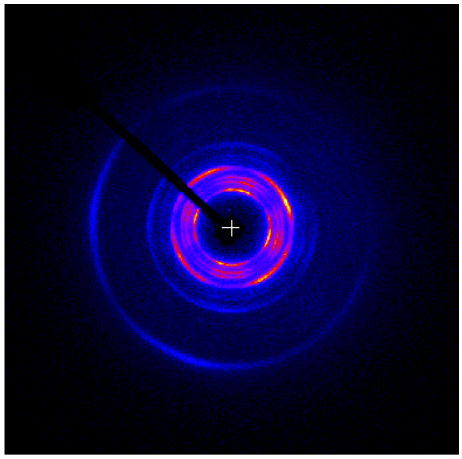


Figure 7.26. Wide Angle X-Ray Diffraction Pattern of PP Fabric Dyed with Vat Blue 1

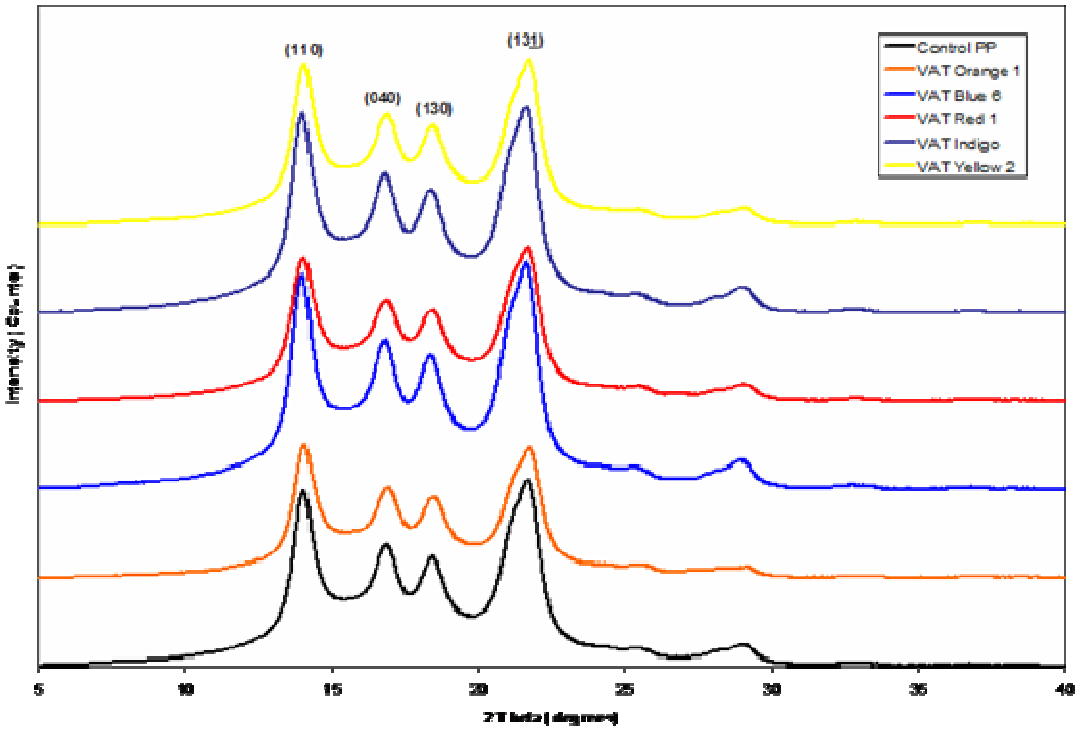


Figure 7.27. Wide Angle X-Ray Diffraction Intensity vs. 2θ Plot for Undyed and Dyed PP Fabrics

Table 7.7. Degree of Crystallinity of Control and Dyed PP Fabrics

Name of Dye	Percent Crystallinity
Control	52.9
Vat Red1	48.7
Vat Yellow 2	50.2
Vat Blue 6	53.1
Vat Orange 1	52.9
Vat Blue 1	50.3

7.13 Pad-Steam Dyeing of Unmodified PP Fabric

An unmodified PP fabric was colored with the certified vat dyes using the developed, simulated pad-steam process (see Section 6.14). The dyed fabrics were measured for K/S values at each dye's respective wavelength of minimum reflectance. Ten measurements were taken for each sample and the average compiled (Table 7.8). Vat Blue 1 exhibited the highest color strength, while the other dyes also showed good color strength and levelness. In fact, the pad-steam dyed fabrics all exhibited better visual levelness than the corresponding batch dyed fabrics.

Table 7.8. K/S Values Obtained at Wavelength of Minimum Reflectance

Name of Dye	K/S at Wavelength of Minimum Reflectance
Vat Red 1	2.7
Vat Yellow 2	3.4
Vat Blue 6	3.6
Vat Orange 1	2.1
Vat Blue 1	8.9

Pad-steam dyed fabrics were evaluated for fastness properties by the procedures described earlier (see Sections 6.9-6.11). The fastness ratings for crocking, washing and dry cleaning are in Tables 7.9-7.11, respectively. The fastness ratings indicated good-to-

excellent resistance of the pad-steam dyed PP fabrics to wet/dry crocking, washing and dry cleaning.

Table 7.9. Crock Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Red 1	4-5	4-5
Vat Yellow 2	4-5	4-5
Vat Blue 6	4	4-5
Vat Orange 1	4-5	5
Vat Blue 1	4-5	4

Table 7.10. Wash Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	5	5	5	4-5	5	4-5	5
Vat Blue 6	5	5	5	4-5	5	4-5	4-5
Vat Blue 1	5	4-5	4-5	4-5	4-5	5	4-5

Table 7.11. Dry Cleaning Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	4-5	5	4	4-5	4-5	4-5	4-5
Vat Blue 6	4-5	4-5	4	4-5	4-5	4-5	4-5
Vat Blue 1	4-5	4-5	4-5	4	4	4	4

7.14 Pad-Dry Heat Dyeing of Unmodified PP Fabric

An unmodified PP fabric sample (10 gms) was dyed with C. I. Vat Red 1 using the simulated pad-dry heat process (see Section 6.15). The dyed sample was measured for its K/S value at the wavelength of minimum reflectance. Ten measurements were taken for the sample and an average was compiled (Table 7.12).

Table 7.12. K/S Value Obtained at Wavelength of Minimum Reflectance

Name of Dye	K/S at Wavelength of Minimum Reflectance
Vat Red 1	2.5

The dyed fabric was evaluated for fastness properties by the procedures described earlier (see Sections 6.9-6.11). The fastness ratings for crocking, washing and dry-cleaning are tabulated in Tables 7.13-7.15, respectively. The fastness ratings quantified good-to-excellent resistance of the pad-dry heat dyed PP fabric to crocking, washing and dry-cleaning.

Table 7.13. Crock Fastness Ratings of PP Fabric Dyed with Vat Red 1

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Red 1	4-5	4-5

Table 7.14. Wash Fastness Ratings of PP Fabric Dyed with Vat Red 1

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	5	5	5	4-5	4-5	4-5	5

Table 7.15. Dry-Cleaning Fastness Ratings of PP Fabric Dyed with Vat Red 1

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	4-5	5	4	4-5	4-5	4	4-5

The amount of dye in the exhaust batch process was standardized at 8 % owf. The amount of dye in the pad-steam and pad-dry heat baths was also taken on the basis of 8% owf and 70% pickup by the PP fabric [38]. A comprehensive plot was prepared for K/S values of all the fabrics dyed with the certified colorants using the exhaust batch, simulated pad-steam and simulated pad-dry heat methods (Figure 7.28) at their respective wavelengths of minimum reflectance.

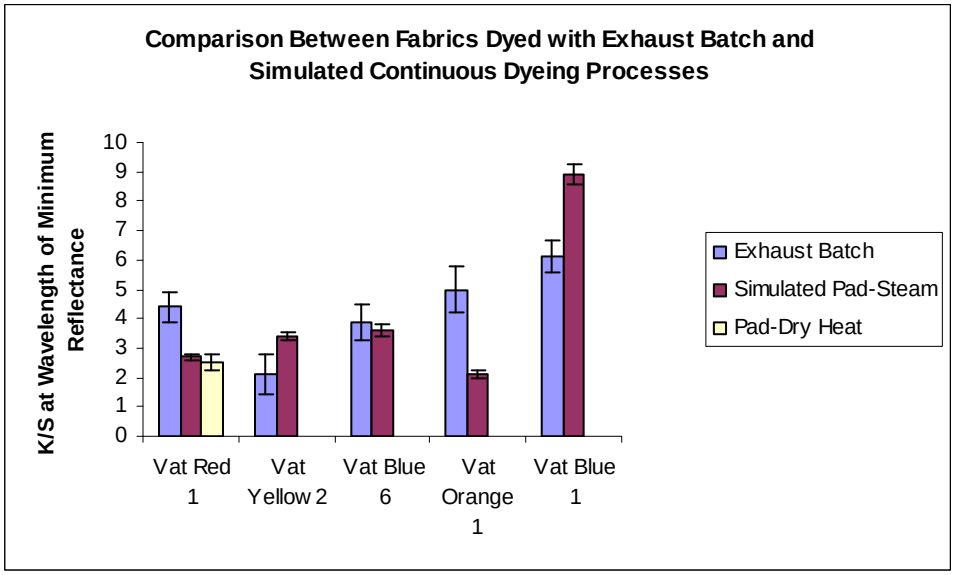


Figure 7.28. Comparison of K/S Values of Vat Dyed PP Fabrics from Exhaust Batch, Simulated Continuous Pad-Steam and Simulated Continuous Pad-Dry Heat Processes

Using the exhaust batch method as the base, the simulated pad-steam method gave higher fabric K/S values for C. I. Vats Yellow 2 and Blue 1. C.I. Vat Blue 6 gave similar fabric color depth in both the exhaust batch and simulated pad-steam processes. C. I. Vats Orange 1 and Red 1 gave lower fabric K/S values in the pad-steam process than in the exhaust batch process. Further, the fabrics colored by the simulated pad-steam

method for all dyes exhibited better levelness than the analogous batch exhaust dyed fabrics, as evidenced by the smaller error bars in Figure 7.28. Similarly, the pad-dry heat process gave a more level Vat Red 1 dyeing than had been achieved with the exhaust batch process. The pad-dry heat and simulated pad-steam processes with Vat Red 1 gave dyed fabrics with similar K/S values.

7.15 Overview of Parallel University of Georgia Research

The University of Georgia (UGA) Research Group (Drs. Nolan Etters, Yiping Lu, Hang Liu and Xialing Wu) screened several additional vat colorants outside the trichromatic series plus orange and indigo group in order to expand the gamut of viable dyes for generic PP coloration via the developed, single-stage, acid leuco batch exhaust process. Several additional vat colorants were demonstrated to have good affinity for the unmodified PP fabric, as evidenced by the CIE L*, a*, b* values obtained from the dyed materials (Table 7.16 [59]).

Table 7.16. Measured CIE L*, a*, b* values of the UGA-Dyed PP Fabrics [59]

C.I. Name of Dye	L*	a*	b*	SPs $(cal/cc)^{1/2}$
Orange 15	83.9	4.4	19.0	16.7
Violet 1	55.8	16.0	-14.0	14.8
Green 1	63.6	-21.2	-0.1	14.9
Red 13	70.1	12.2	-2.3	14.8
Brown 1	54.9	9.2	5.4	19.3
Yellow 33	79.7	7.9	47.5	16.0

After evaluating wash fastness properties of the dyed fabrics, Wu and Etters [60] certified that C. I. Vats Red 15 (SP 14.4 $(cal/cc)^{1/2}$, Table 7.1), Green 1 (SP 14.9 $(cal/cc)^{1/2}$) and Violet 1 (SP 14.8 $(cal/cc)^{1/2}$) were viable colorants for dyeing PP in the developed batch exhaust process. The additional certified vat dyes all had low SP's in

their acid leuco forms, correlating with the findings of the work reported herein. The researchers also demonstrated that Vat Brown 1 suffered low fixation upon soaping the dyed fabrics, correlating with the lower K/S value of completed PP fabric dyed with Vat Brown 1 (Table 7.2).

CHAPTER 8: CONCLUSIONS

Solubility parameter and molecular dynamics simulation approaches were developed to screen viable vat dye candidates for generic PP aqueous dyeing, and the dyes targeted as viable candidates by the theoretical techniques provided excellent experimental correlations, e.g., high color yields, in dyeing PP fabrics by the optimized acid leuco vat process.

A viable method to commercially aqueous batch dye generic, unmodified PP fiber textiles in a conventional process has been developed for a certified trichromatic series (red, yellow and blue) plus orange of vat dyes with adequate fastness properties to washing, crocking and dry-cleaning in their acid leuco forms: C. I. Vats Red 1, Yellow 2 and Blue 6 plus Orange 1. The same method was shown to adequately color PP textiles with C. I. Vat Blue 1 (Indigo) as a stand-alone colorant with adequate fastness properties to washing, crocking and dry-cleaning to produce the popular "denim" shade. The developed single-stage acid leuco method for dyeing generic PP fabrics at pH 7 provided good fastness properties and good color yields without fiber "ring-dyeing."

Of the vat dyes currently available on the commercial market, C. I. Vat Dyes Orange 1, Yellow 2, Red 1 and Blue 1, all possessing low solubility parameters closest to that of generic PP's 8.1 $(cal/cc)^{1/2}$, were demonstrated to be viable candidates for generic PP fiber coloration, while C. I. Vat Blue 6 was deemed a marginal candidate. However, Vat Blue 6 was the best-performing blue vat dye available outside of Vat Blue 1, and since the latter was so easily air-oxidized compared to the other candidates for the

trichromatic series and was thus incompatible with them, Vat Blue 6 was judged sufficient in performance to move the technology forward into practice.

An exhaustive survey of blue vat dye structures in the Colour Index yielded one colorant that possessed the proper solubility parameter and heat of mixing with PP characteristics: C. I. Vat Blue 8. However, the colorant is no longer commercially available on the world market, but with the viable aqueous PP coloration process now developed, vat dye manufacturers will have incentives to bring Vat Blue 8 back into production.

Experimentally-determined thermodynamic parameters such as affinity of dyeing and heat of dyeing indicated the significant degree of interaction between the certified acid leuco vat dyes and generic PP fiber, e.g., the derived negative heats of dyeing and low entropies of dyeing. Adsorption isotherms confirmed high saturation values of the certified dyes in the fiber phase, resulting in good color yields on the dyed fabrics. Dyeing rate plots with colorant combinations exhibited similar dyeing rate profiles to those of the component dyes, confirming the compatibility of the certified vat dye mixtures (critical for wide shade development of PP products).

Cross-sectional microtomes of PP fiber bundles dyed in the loose stock form proved complete dye diffusion throughout the fiber structures, i.e., “ring dyeing” was absent in the developed acid leuco vat dyeing process. Tensile testing and X-ray diffraction results quantified the full retention of mechanical and solid-state structure properties of the generic PP fiber after the dyeing process.

Parallel batch exhaust dyeing research conducted at the University of Georgia certified three additional structures for coloration of generic PP by the single-stage, acid

leuco vat dyeing process: C. I. Vats Red 15, Violet 1 and Green 1. All three dyes possessed low SP's in their acid leuco forms (14.4, 14.8 and 14.9 (cal/cc) $^{1/2}$), respectively), correlating well with the theoretical and experimental findings of the work reported herein.

The developed, simulated pad-steam dyeing method for vat dyeing of generic PP fabric gave higher fabric K/S values than the analogous batch dyed fabrics for C. I. Vats Yellow 2 and Blue 1. C.I. Vat Blue 6-dyed fabrics exhibited similar color depth in both the exhaust batch and simulated pad-steam processes. Fabrics dyed with C. I. Vats Orange 1 and Red 1 by the simulated pad-steam process exhibited lower K/S values than analogous fabrics colored in the exhaust batch process. The simulated pad-steam method for all dyes produced fabrics exhibiting better dye level than analogous fabrics colored by the batch exhaust method, a reflection of the poor bath circulation and pumping pressure of the Roaches Lab Machine through the mounted, multi-layered, tightly woven PP fabric.

The developed, simulated pad-dry heat dyeing method for C. I. Vat Red 1 on generic PP produced a fabric with a similar K/S value to that generated by the simulated pad-steam method with the same dye at analogous pad bath formulations. Dyed fabrics produced by both the pad-steam and pad-dry heat processes exhibited adequate fastness to wet/dry crocking, washing and dry cleaning, thus qualifying the developed continuous processes.

CHAPTER 9: RECOMMENDATIONS

- Develop theoretical model chemical structures of vat dyes having low solubility parameters/mixing energies, and synthesize the model vat dyes. The synthesized dyes should then be screened for their abilities to color unmodified PP fabric in the developed acid leuco vat dyeing processes.
- Screen additional, commercially-available vat colorants on the basis of solubility parameter calculations/mixing energy predictions to expand the list of potentially viable candidates for the developed PP dyeing processes.
- Request that vat dye manufacturers synthesize and supply C. I. Vat Blue 8 to allow experimental evaluation of it as a more-viable blue colorant for the trichromatic series in comparison to C. I. Vat Blue 6.
- Dye unmodified PP flat fabrics using combinations of the trichromatic series plus orange colorants in light, medium and dark shades with the optimized pad-steam process.
- Dye the unmodified PP fabric using the pad-dry heat method with all the colorants of the trichromatic series plus orange group, using single as well as combinations of dyes. C. I. Vat Blue 1 should also be evaluated with this process.
- Vat dye generic PP tufted carpet constructions and technical textiles with all the certified colorants using the three developed processes: batch exhaust, pad-steam and pad-dry heat.

- Pilot process scale-up trials of the optimized batch exhaust, pad-steam and pad-dry heat vat dyeing methods should be conducted for the four projected products (flat, towel and industrial textiles, plus tufted carpets), and further optimization of the processes effected if necessary.

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